Process Synthesis For a Sustainable Energy Future

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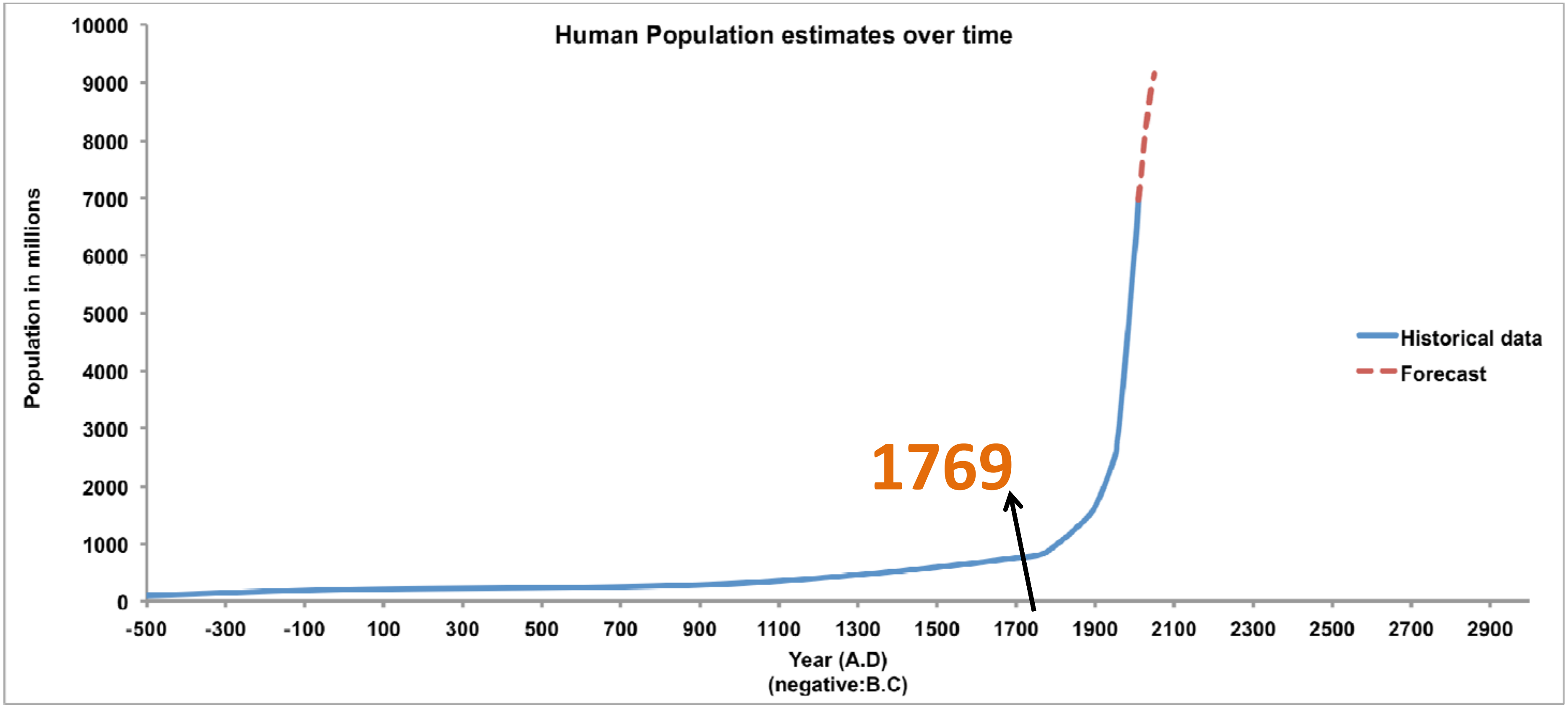
Human Population Growth



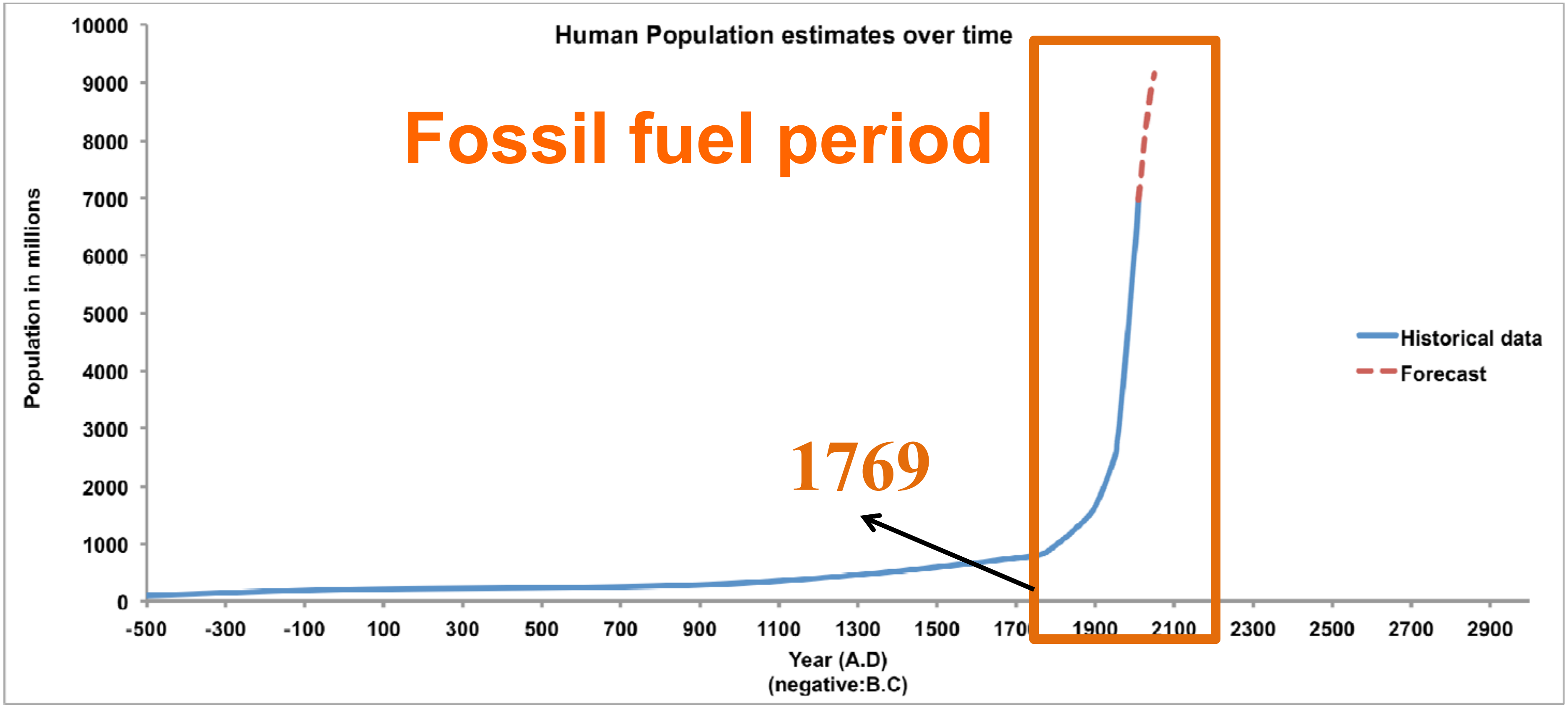
1769

Data source: Wikipedia & UN

James Watt and his 1769 steam engine

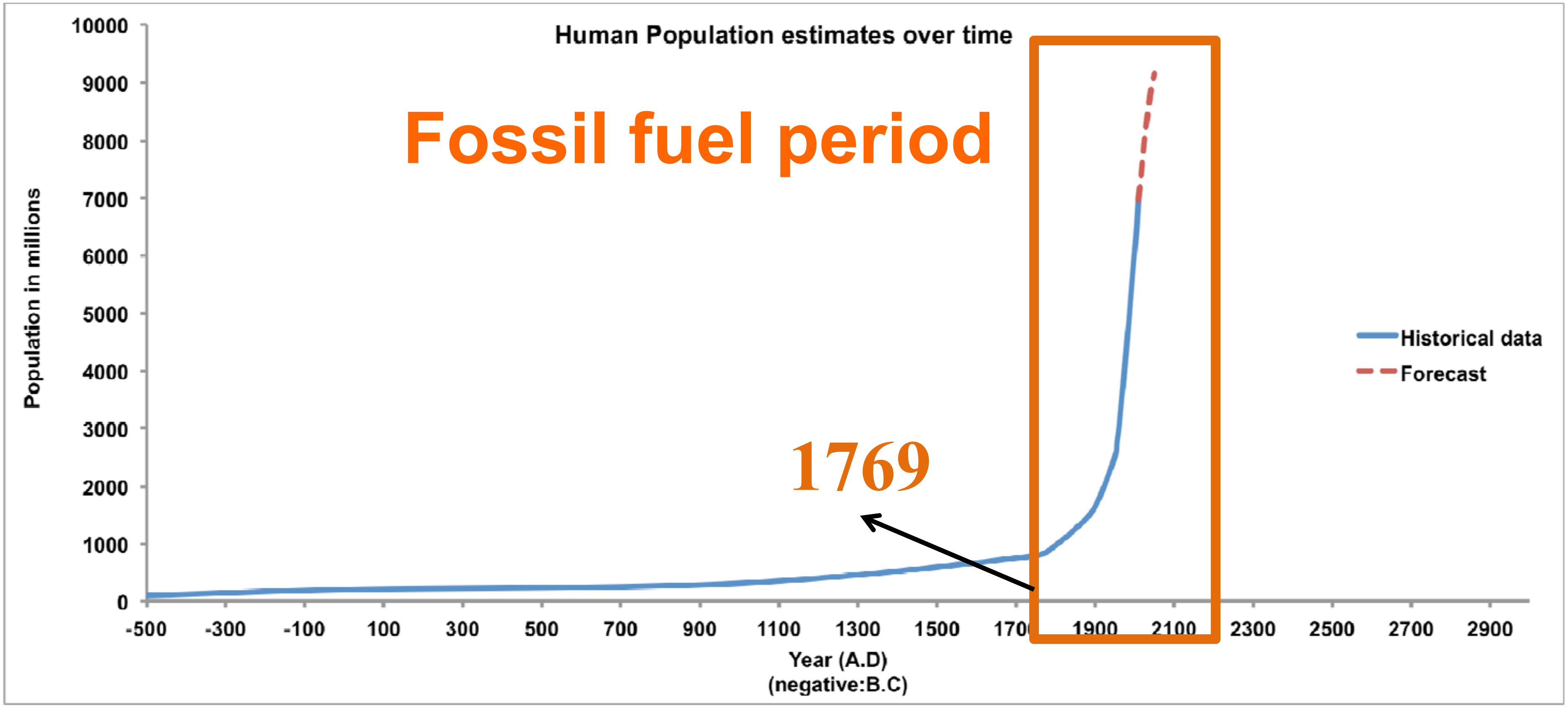
Source: David J.C. Mackay 2009

Energy: Fundamental to Our Lives!



Data source: Wikipedia & UN
Kremer M, *The Quarterly Journal of Economics*, 108, 1993

Energy: Fundamental to Our Lives!



Fossil fuel period

1769

Therefore, we must understand energy transformation and use issues to develop alternative energy strategies

Data source: Wikipedia & UN

Kremer M, *The Quarterly Journal of Economics*, 108, 1993

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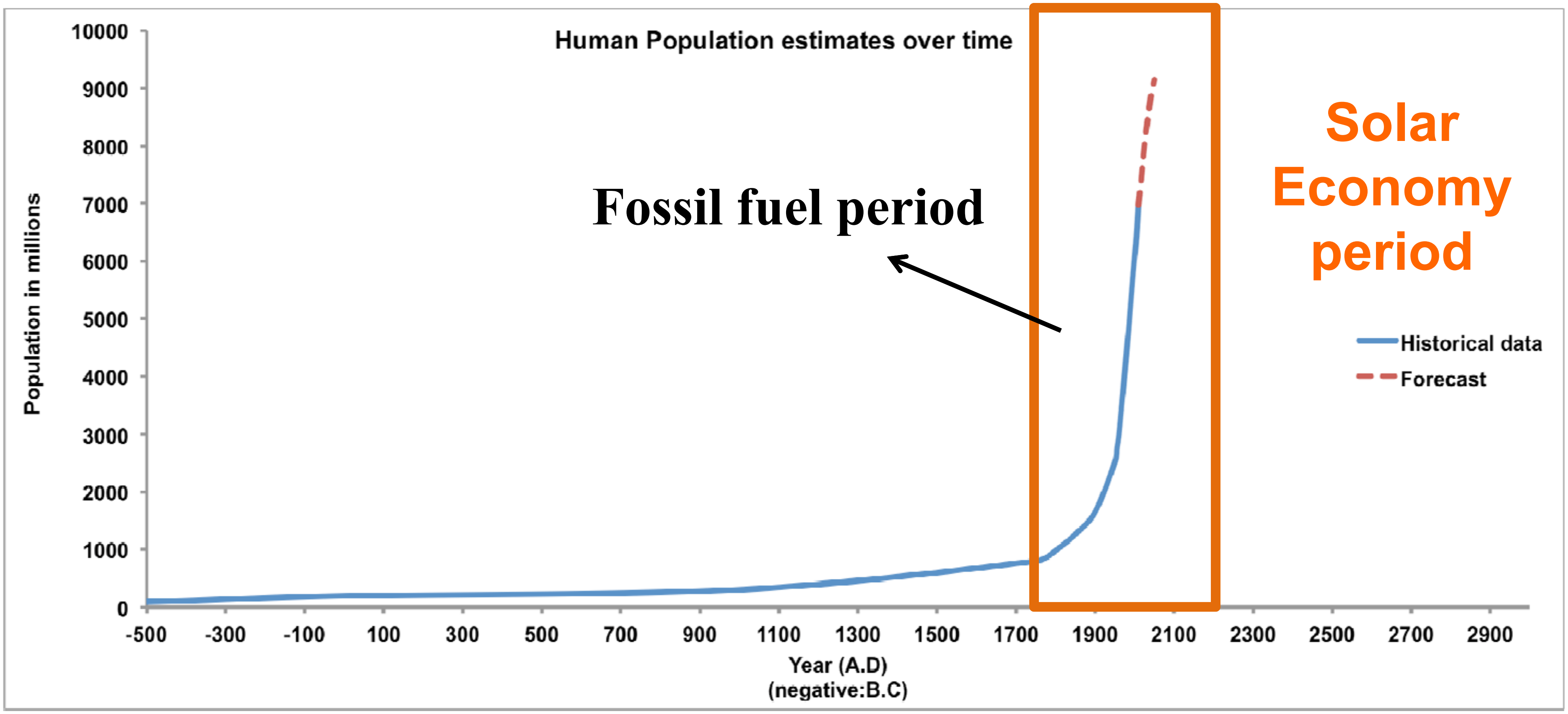
Beyond Fossil Fuels: Solar Economy



Fossil fuel period

Solar Economy period

Data source: Wikipedia & UN

Why Solar Energy?

- Solar energy incident on earth in 1 hour[1]

  ~ 4.3×10^{20} J

- 2012 World primary energy consumption[2]

  ~ 5.1×10^{20} J

Solar is the only easily available energy source that can alone meet all the energy needs.

1. Lewis and Nocera, PNAS, 2006
2. BP Statistical Review of World Energy, 2012

Essence of Solar Economy

Transform and use solar photons on a much smaller time scale ~ O(10^3-10^6 s)!

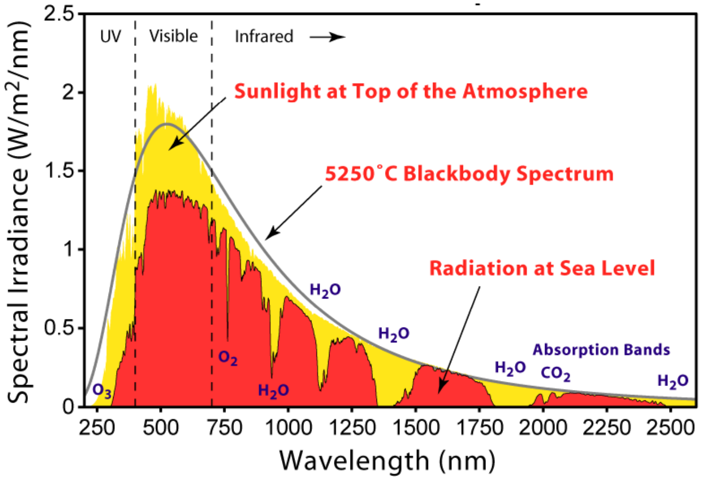
1. How Dense is Solar Energy?

~10 gallons per minute

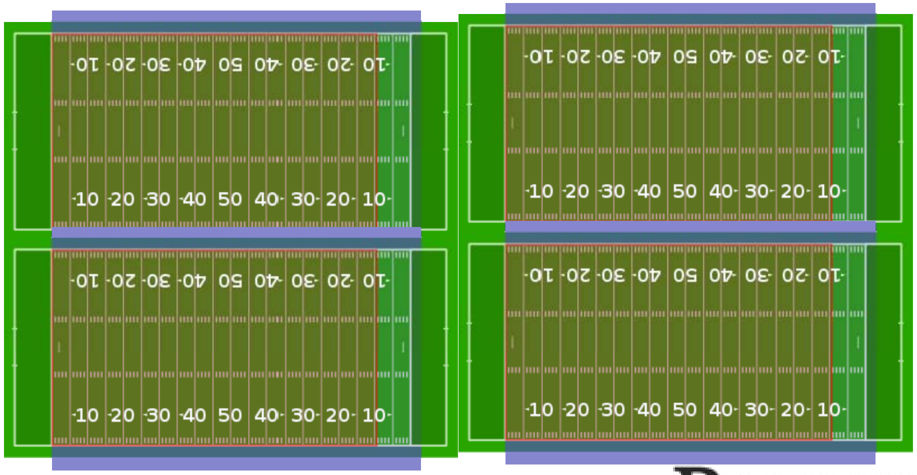
Or

~20 MW of power supply

1000 W/m^2



Area: ~20, 000 m^2



Source: epa.gov, Wikipedia

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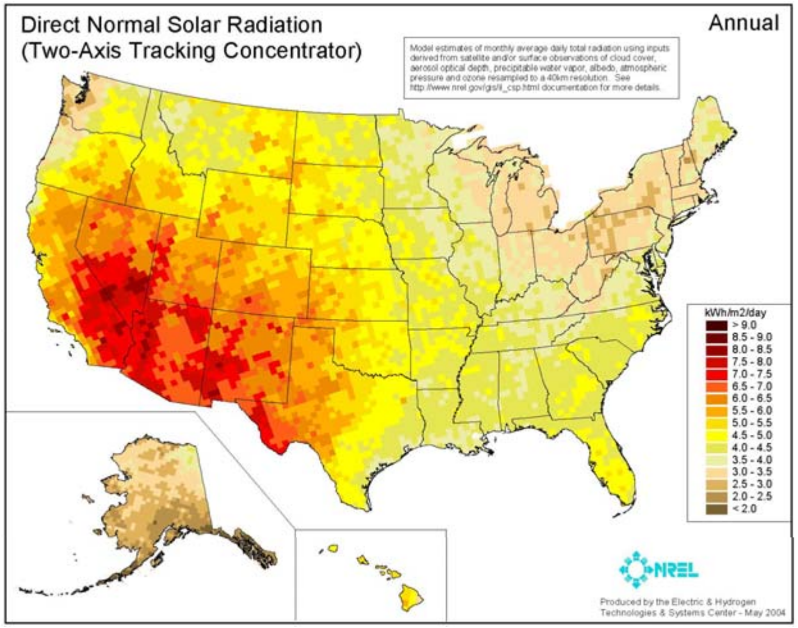
Observation 1

Low density of solar energy is a challenge for use

2. Availability of Sunlight

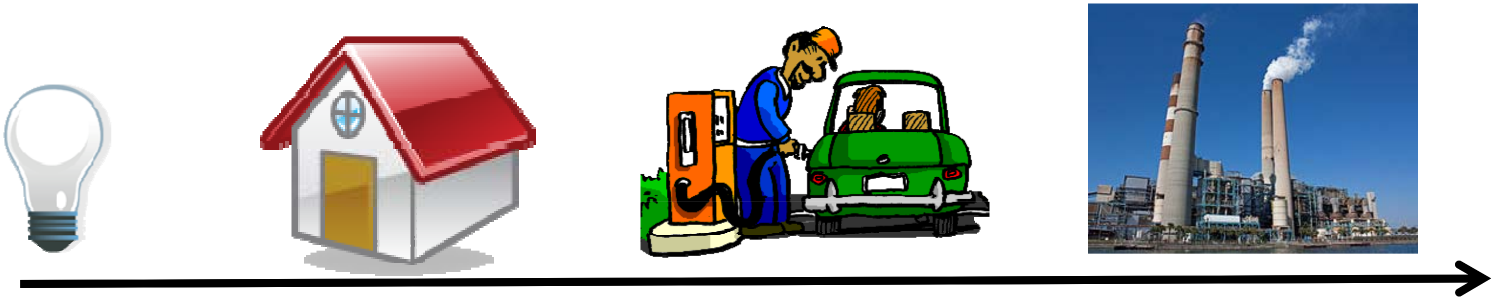
Intermittency

Geographic Variability



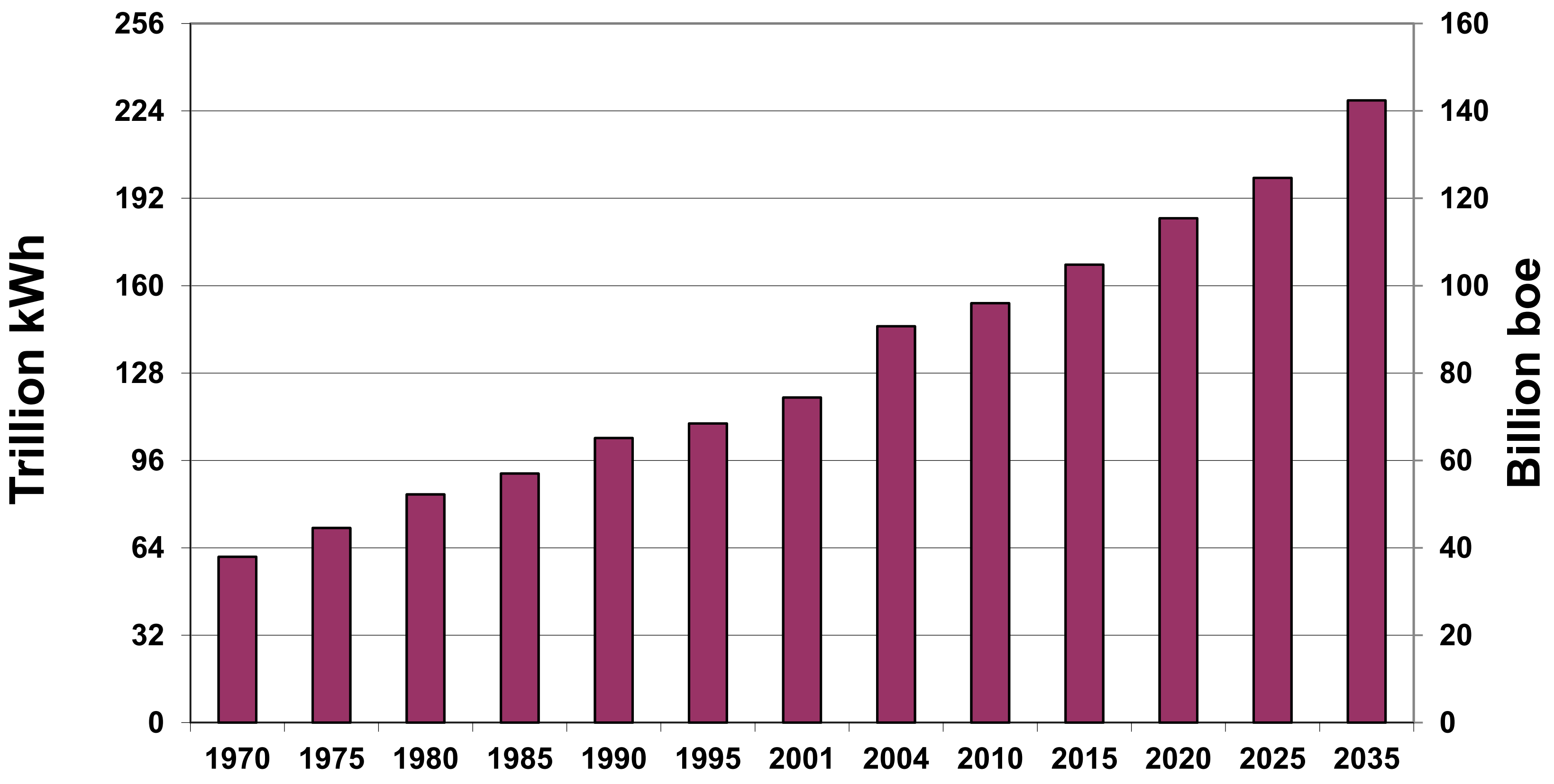
Source: nrel.gov, NASA

Observation 2:
Energy storage needed at all levels



~10^2 W ~10^3 W ~10^6 W ~10^8 W

3. Large Scale Energy Requirement



- **World primary energy usage rate in 2007 was 14.8 TW**
- **By 2050, the usage rate could be 28 TW**

Consumption rate could double!

Adaptation : EIA

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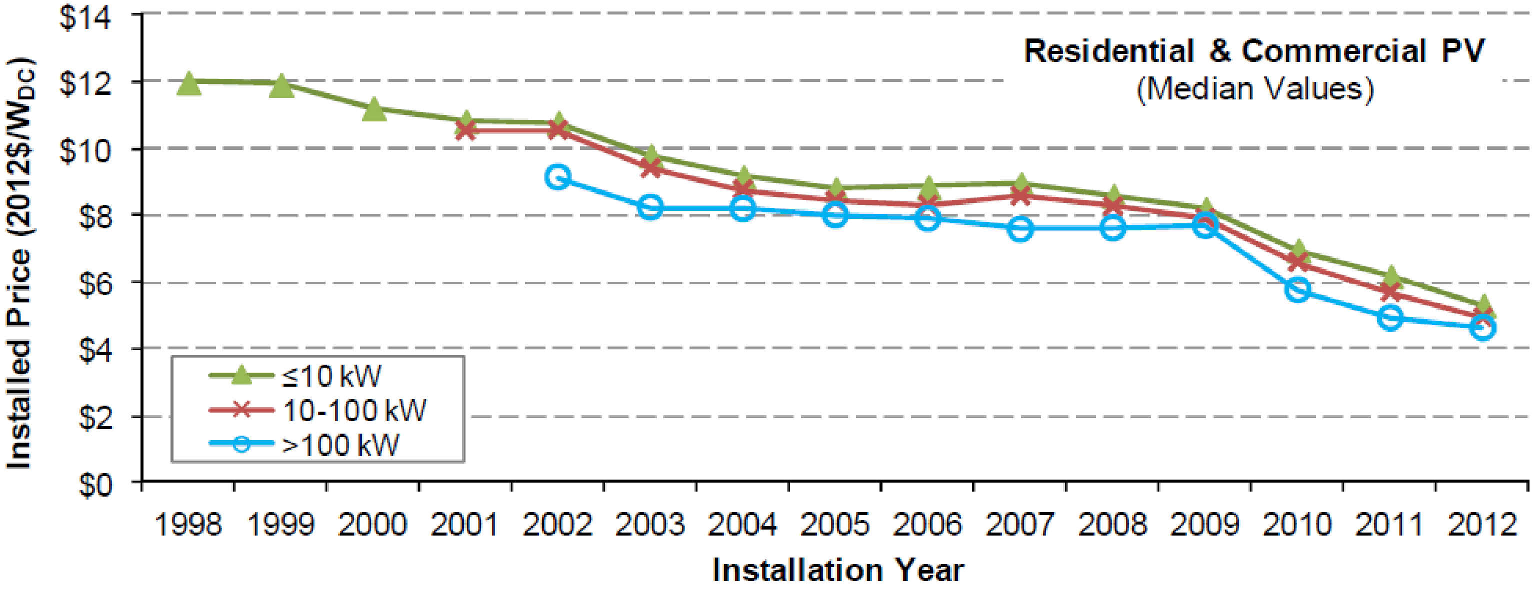
Observation 3

Large-scale only possible if cost-effective

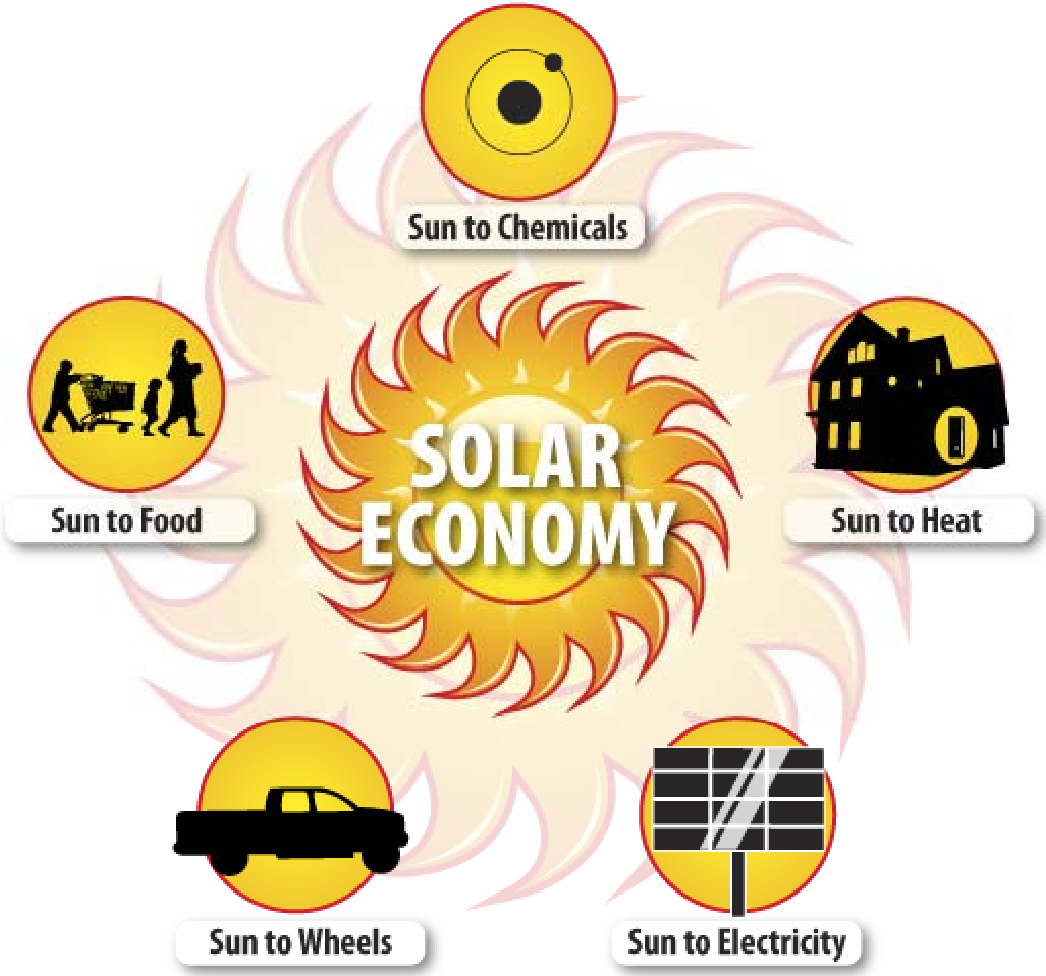


Barbose, Darghouth, Weaver & Wiser, LBNL,2013

Observation 4

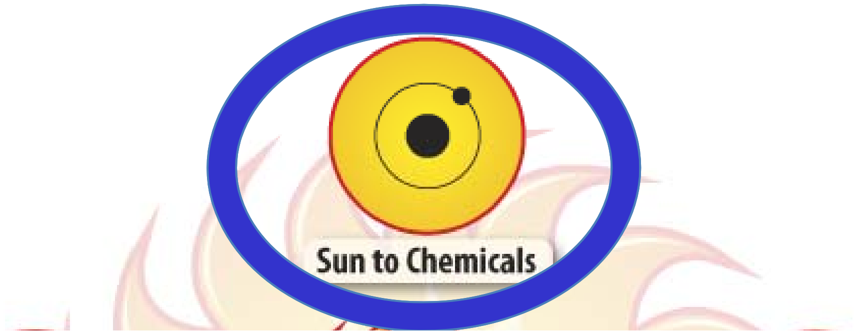
Harnessing solar energy efficiently is vital

Solar Economy Vision



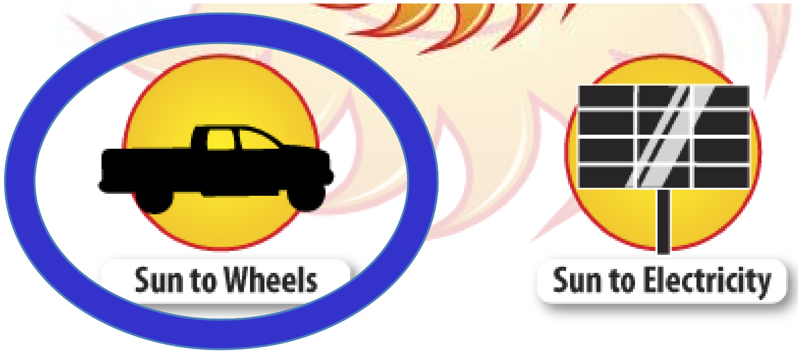
Agrawal and Singh, ***Annual Rev. Chem. Bio. Eng.*** **, 2010**

Fuels and Chemicals



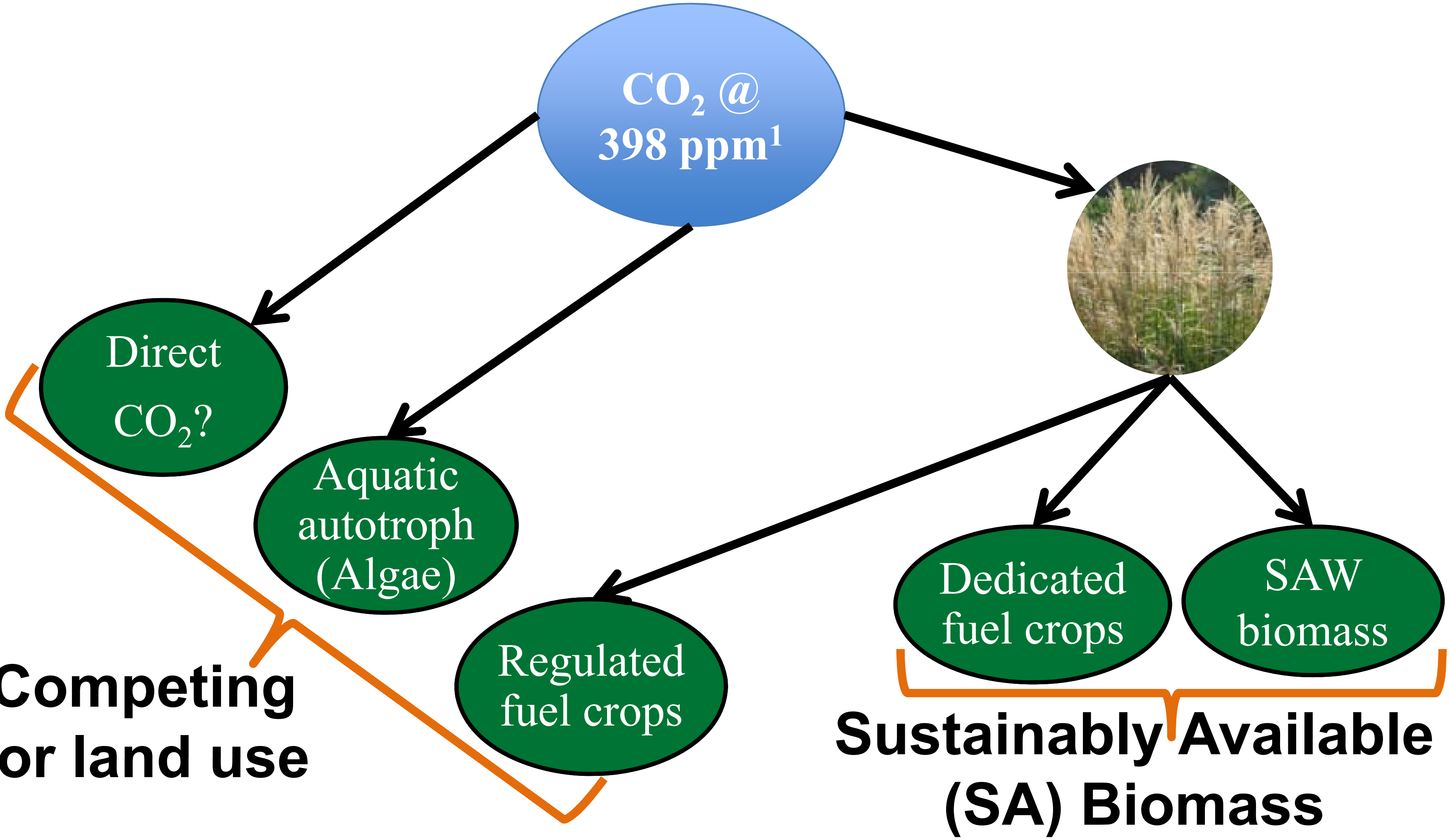
… possibly need **renewable carbon sources**…

…as well as **Hydrogen**…



Agrawal and Singh, *Annual Rev. Chem. Bio. Eng.* , 2010

Renewable Carbon Sources



CO_2 @ 398 ppm[1]

Direct CO_2?

Aquatic autotroph (Algae)

Regulated fuel crops

Dedicated fuel crops

SAW biomass

Competing for land use

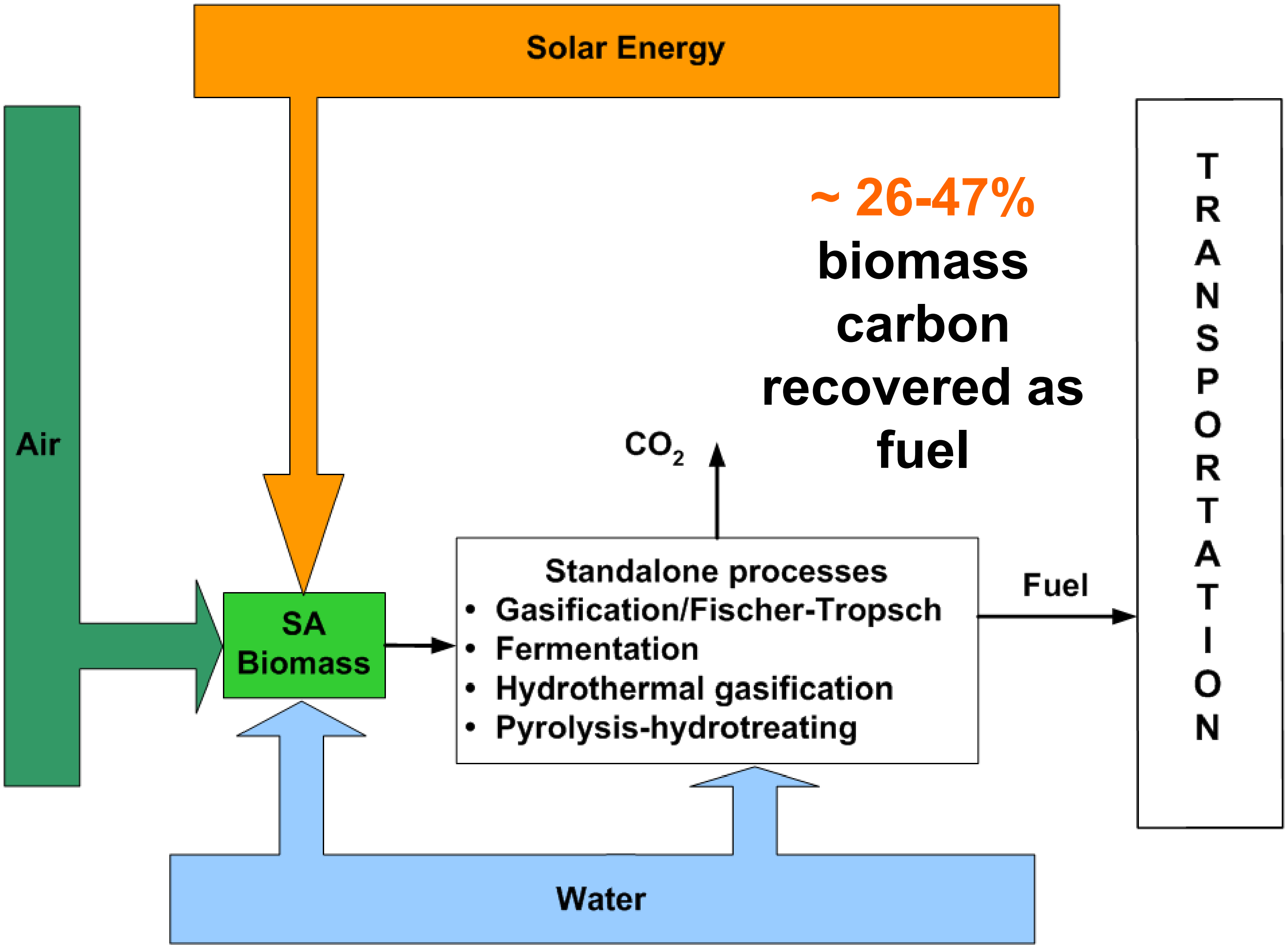
Sustainably Available (SA) Biomass

[1] July 2013: http://www.esrl.noaa.gov/gmd/ccgg/trends/mlo.html

Observation 5

SA biomass = primary energy+ carbon source

Biomass-to-Fuel: Carbon Recovery



Standalone processes
- Gasification/Fischer-Tropsch
- Fermentation
- Hydrothermal gasification
- Pyrolysis-hydrotreating

~ 26-47% biomass carbon recovered as fuel

SA Biomass= sustainably available biomass

Singh, Delgass, Ribeiro and Agrawal, *Environ. Sci. Tech.*, 2010

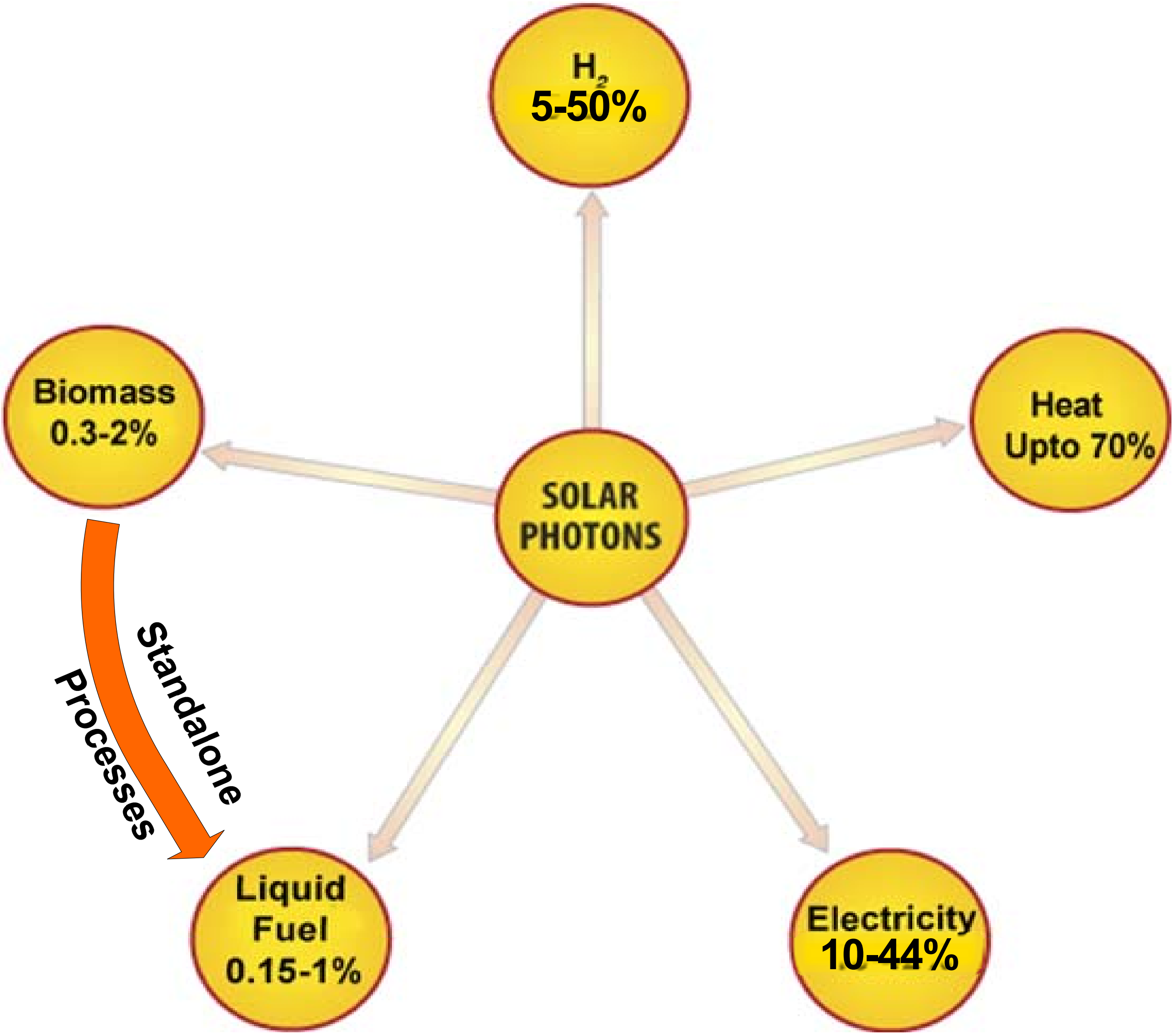
Standalone Processes+ SA Biomass for US Transportation

- **Sustainably available biomass potential= 498 Million tons/yr[1]**
- **Transportation fuels use in the USA, 2011 =12.68 Mbbl/day[2]**

12-20% (1.6-2.6 Mbbl/day) of current US transportation demand produced using SA biomass with standalone processes

1. **Liquid transportation fuels NRC report, 2010**
2. **Davis *et al.*, Transportation energy data book, 2012**

Solar conversion efficiencies



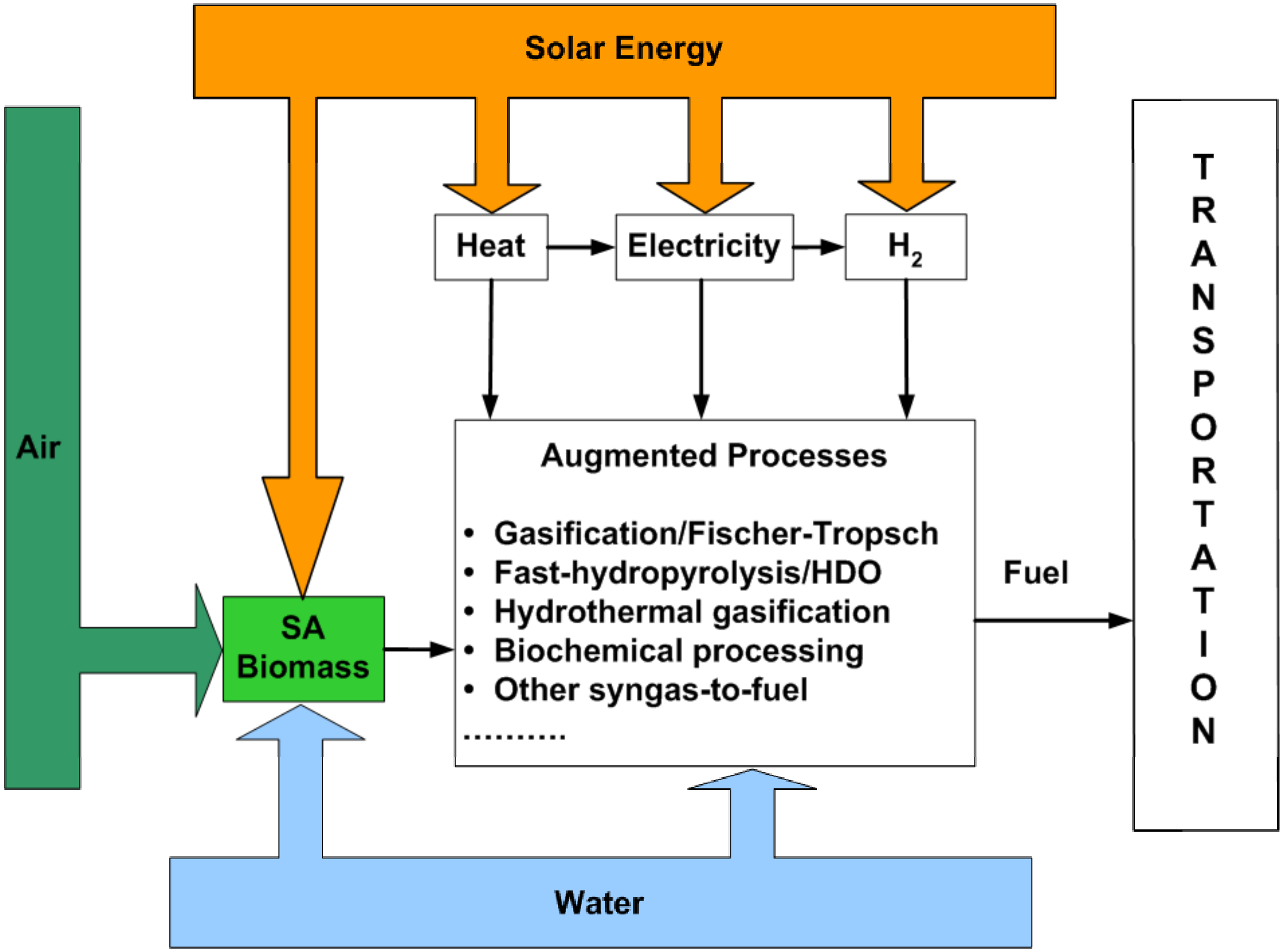
~ 50% efficient

Observation 6

Biomass is primarily a carbon source

Avoid using biomass for non-carbon needs (heat/electricity/H_2)

Augmented Biomass Conversion



Augmented Processes

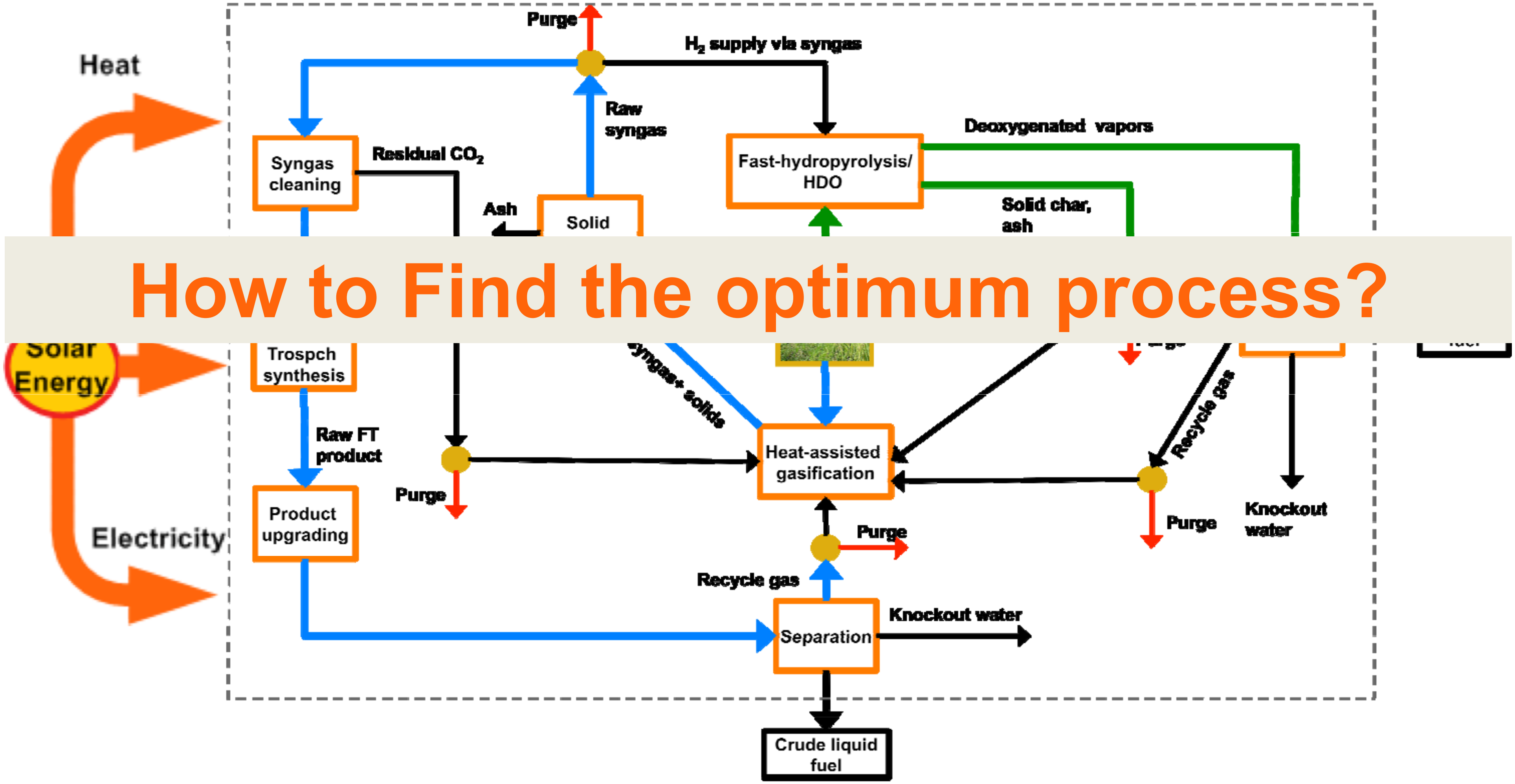
- Gasification/Fischer-Tropsch
- Fast-hydropyrolysis/HDO
- Hydrothermal gasification
- Biochemical processing
- Other syngas-to-fuel

……….

Up to 100% biomass carbon recovery possible

Singh, Delgass, Ribeiro and Agrawal, *Environ. Sci. Tech.*, 2010

Systematic Augmented Process Synthesis



How to Find the optimum process?

FT=Fischer-Tropsch; HDO= hydrodeoxygenation

Augmented process synthesis: MINLP model

$$Min\ Q_{solar} = \frac{Q_{H2}}{\eta_{STH_2}} + \frac{Q_{Heat}}{\eta_{STHe}} + \frac{W_{elec}}{\eta_{STE}}$$

…. Objective function

subject to,

$$f(\mathbf{x}, \mathbf{y}) = 0$$

…. Mass, Energy balance, thermodynamic models

$$h(\mathbf{x}, \mathbf{y}) \leq 0$$

…. Inequalities (split fractions, conversion etc.)

$$carbon_{eff} \geq carbon_{target}$$

…. Target carbon recovery level

$$\mathbf{x}^L \leq \mathbf{x} \leq \mathbf{x}^U$$

$$\mathbf{y} = \{0, 1\}$$

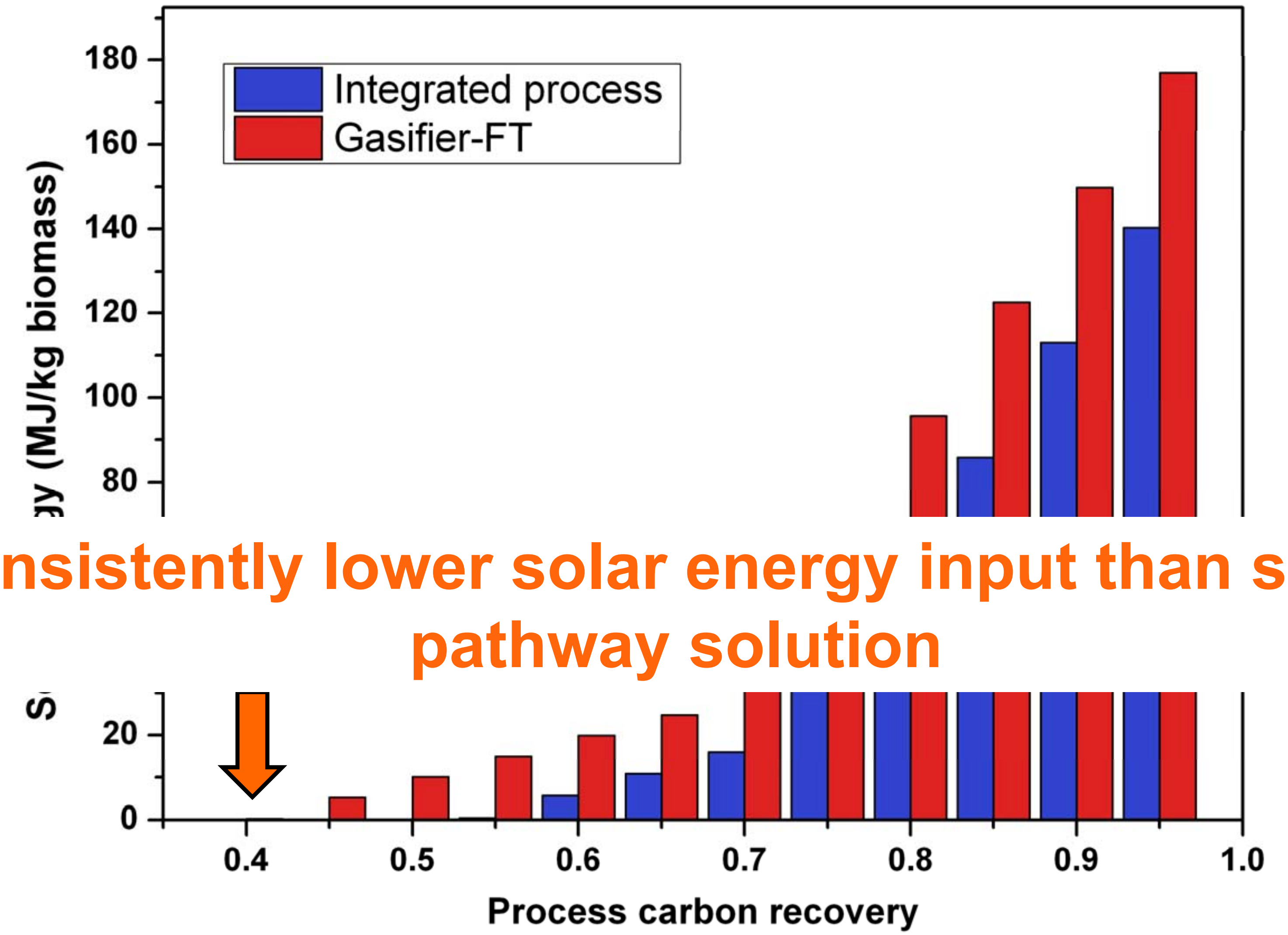
…. Variable bounds

- **Branch and Bound based global optimization algorithm (BARON[1])**

MINLP= Mixed Integer Nonlinear Programming

1. Tawarmalani and Sahinidis, *Math Programm.* , 2005

Benefit of Simultaneous Heat, Mass & Power integration



Consistently lower solar energy input than single pathway solution

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Sun-to-H_2 = 6.2%, Sun-to-heat= 37.5%, Sun-to- electricity =10%

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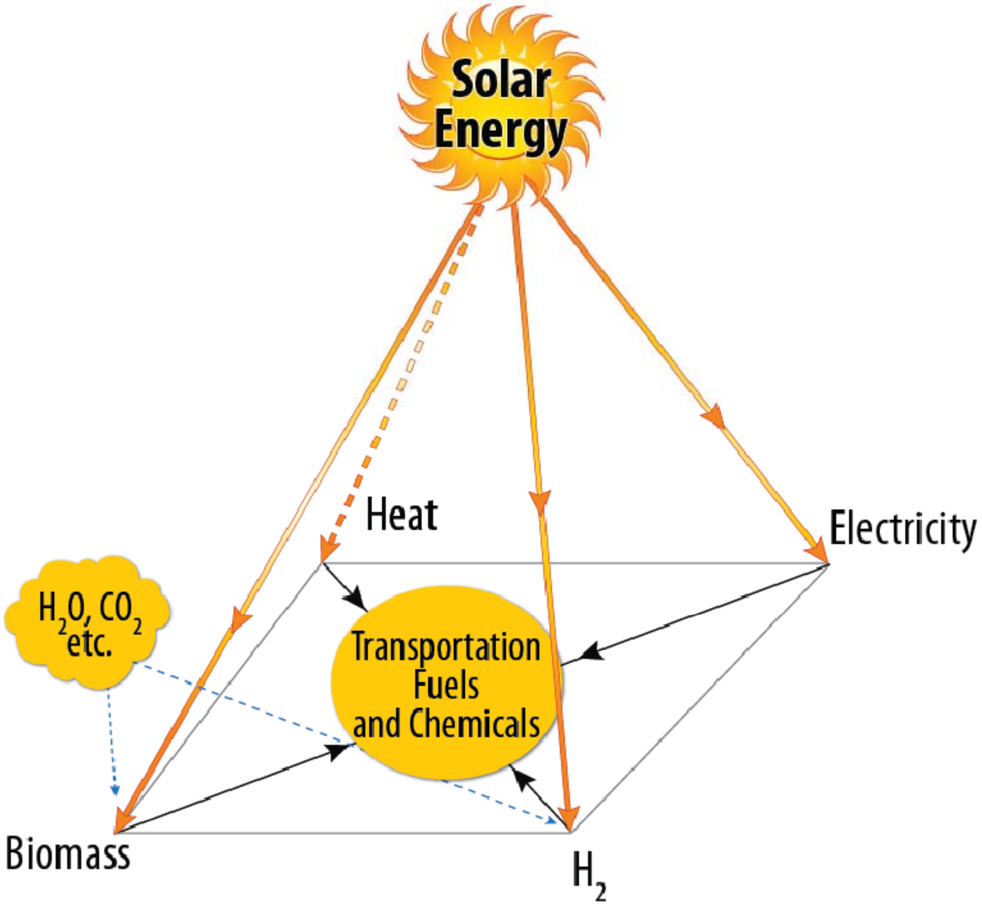
Observation 7

Systems analysis critical for biomass utilization



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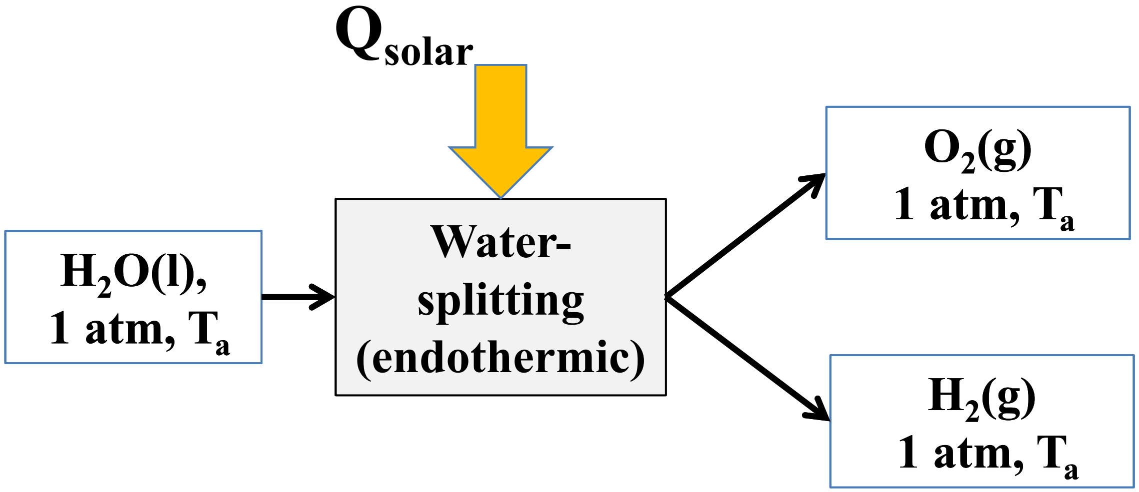
Observation 8

Efficient supply of solar hydrogen needed

What is the Most Efficient Process for Solar Hydrogen?



Q_{solar}

$H_2O(l)$, 1 atm, T_a

Water-splitting (endothermic)

$O_2(g)$ 1 atm, T_a

$H_2(g)$ 1 atm, T_a

$$\text{Sun-to-H}_2\text{ efficiency (\%)} = \frac{\text{LHV of H}_2\text{ produced from land}}{\text{Incident annual solar energy on the land}} \times 100$$

- Light → Photochemical
- Heat → Thermochemical
- Heat or light →Electricity → Electrolysis

Solar Energy Input as Light: Spectrum

Photochemical process are limited by fraction of solar spectrum absorbed

Theoretical Sun-to-H_2 efficiency:
31 - 46%
(single or double band-gap photosystems)[1]

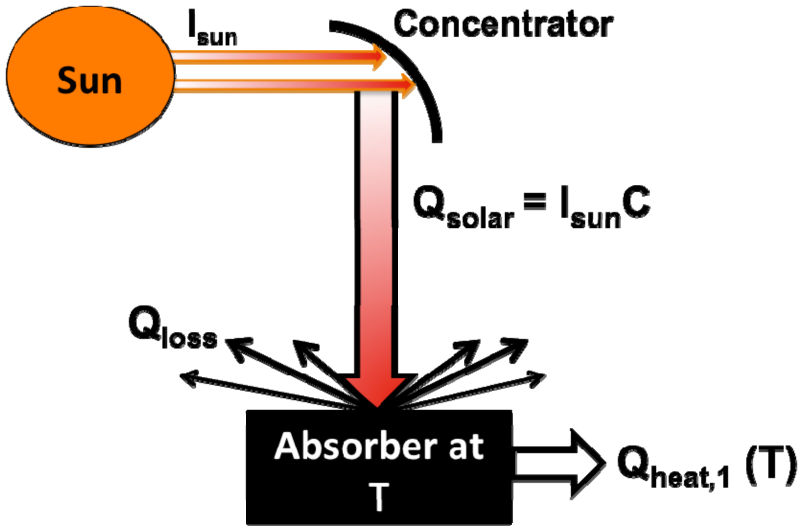
[1] **Bolton et al., *Nature* , 1985**

Sun-to-H_2 thermochemical process

Use solar energy as heat to utilize the entire solar spectrum

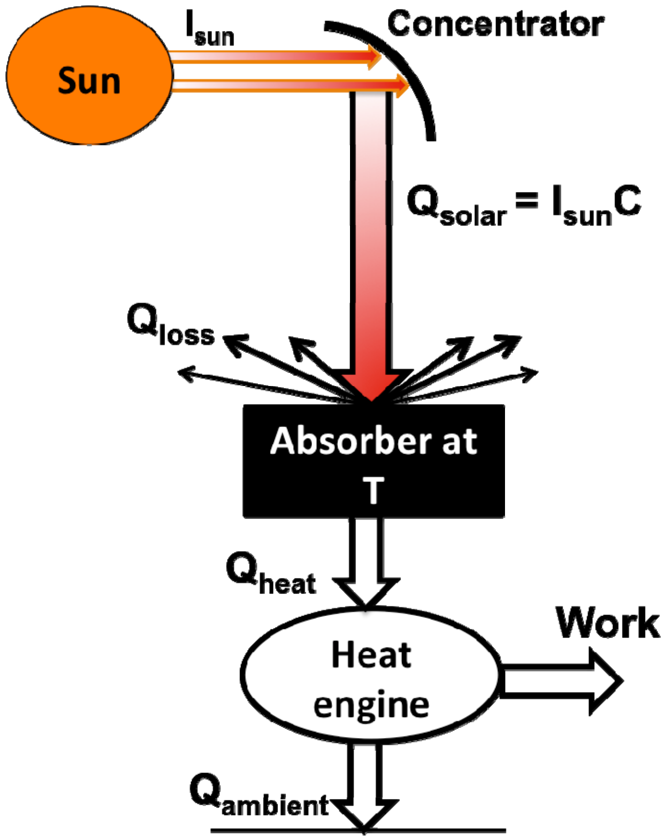
Using Solar Energy as Heat

Direct (Thermal)



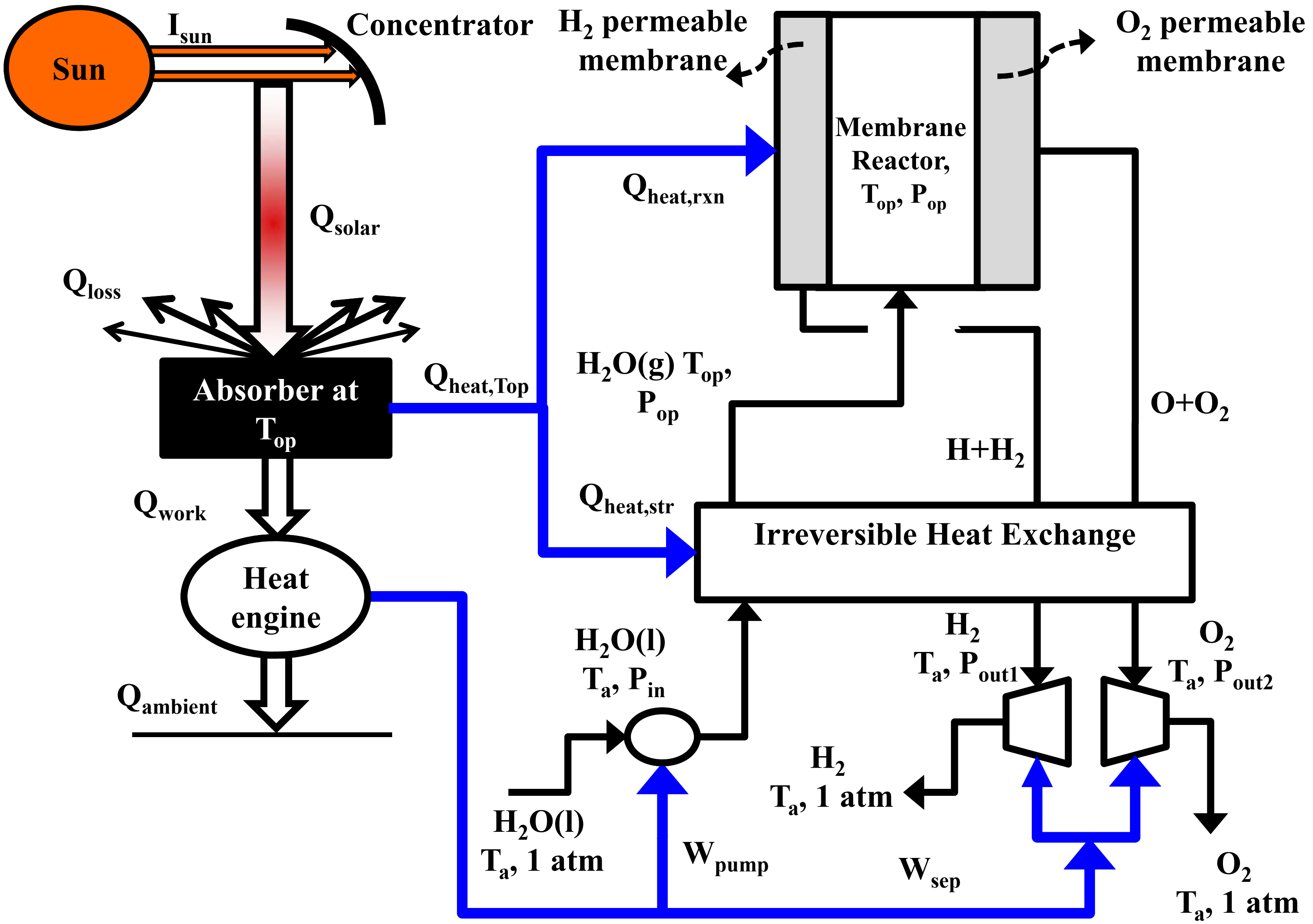
OR

Indirect (Electrolytic)



Practical Thermal Water-splitting

heat exchange (ΔT_{min})+ high pressure (P_{op})



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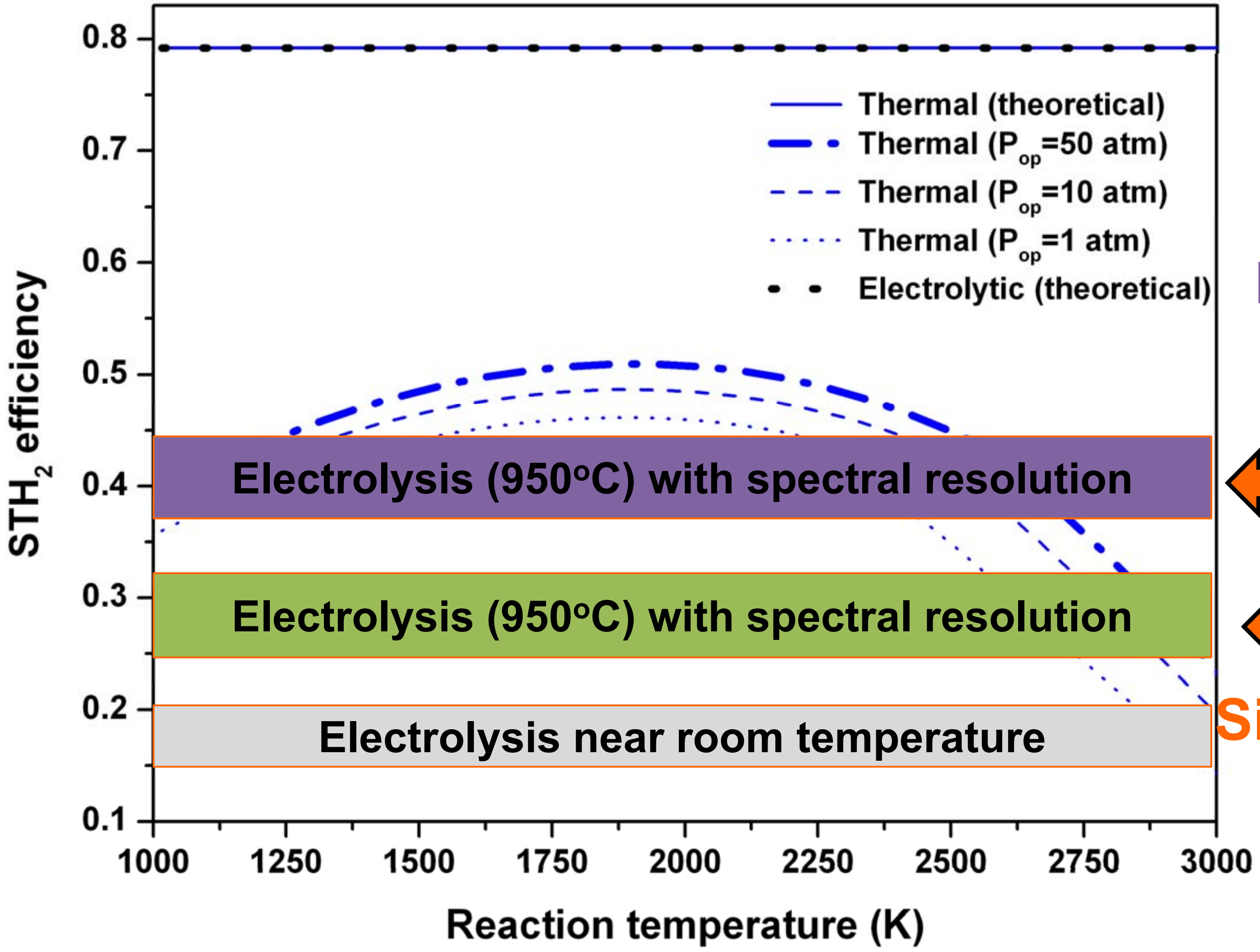
Thermal vs Electrolytic Water-splitting



Electrolysis (950°C) with spectral resolution

Electrolysis (950°C) with spectral resolution

Electrolysis near room temperature

Multijunction PV
η_{PV} =44%

38-45%

25-32%

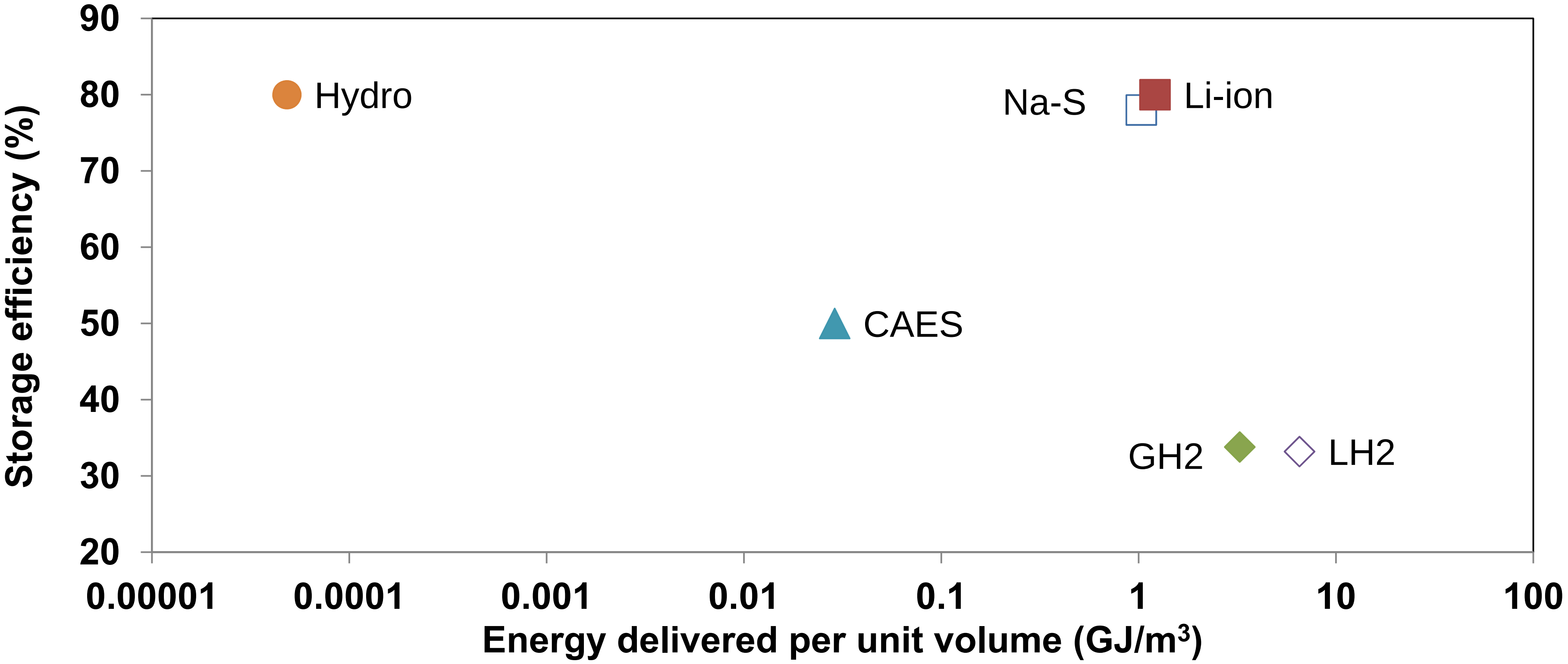
Single junction PV
η_{PV} =29%

C=8000, Ω_{ratio} = 5, $\Omega_{optical}$ =80%, Ω_{Carnot} =50%, Ω_{Comp} =70%, $\Omega_{hte,loss}$ =0.49-0.17, $\Omega_{dp,loss}$ =10%, ΔT_{min} =0 K

Observation 9

Achievable STH_2 efficiency of 35-50% possible!

But Storing Energy as H_2 is Inefficient…



Need- high energy density and storage efficiency solutions!

Reference: EPRI report on Storage Technologies, 2010
Hydro= pumped hydroelectric power, CAES= compressed air energy storage

Storing Energy at the Grid-level

For Baseload renewable power supply

What is Grid-level Storage?

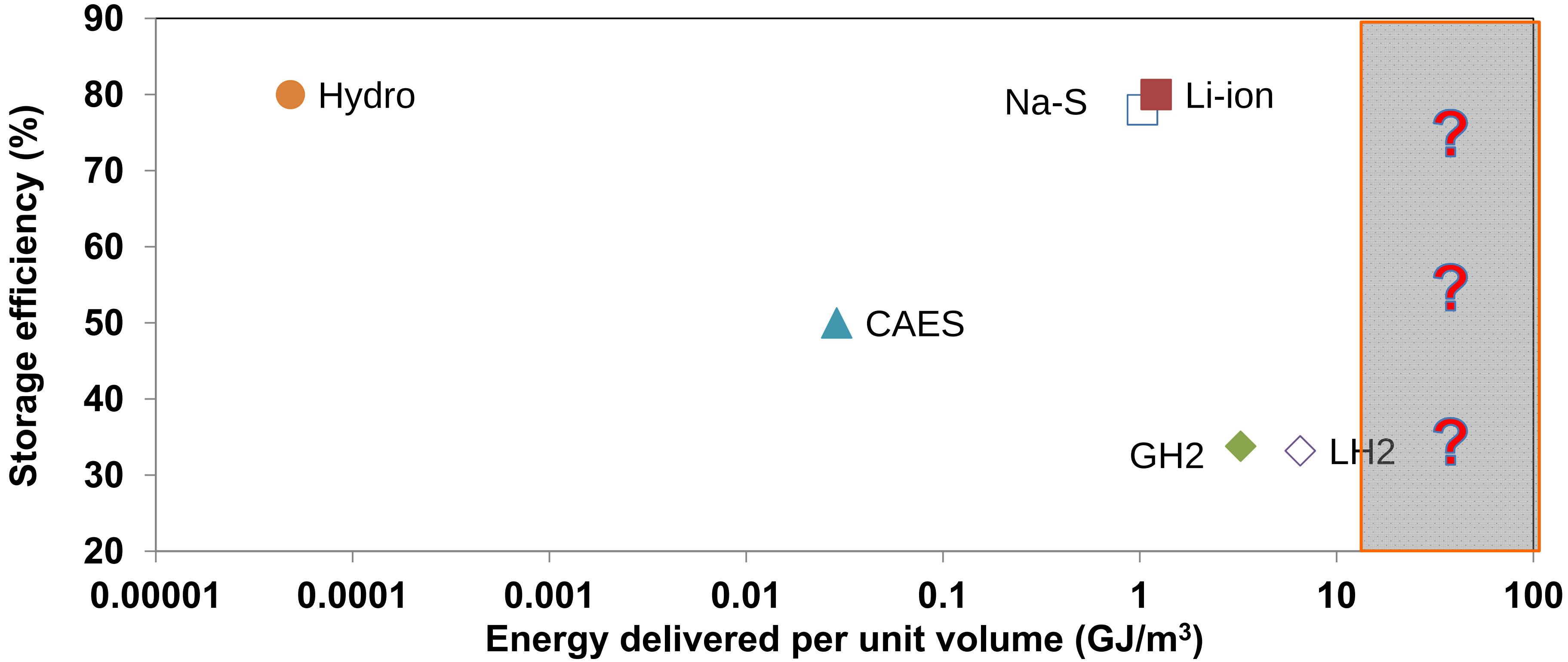
Sunlight available ~1/5th of the day in US

Average 100 MW_{elec} supply…..

…. ~ 2 GWh of electrical energy storage

High density critical for Grid-level storage

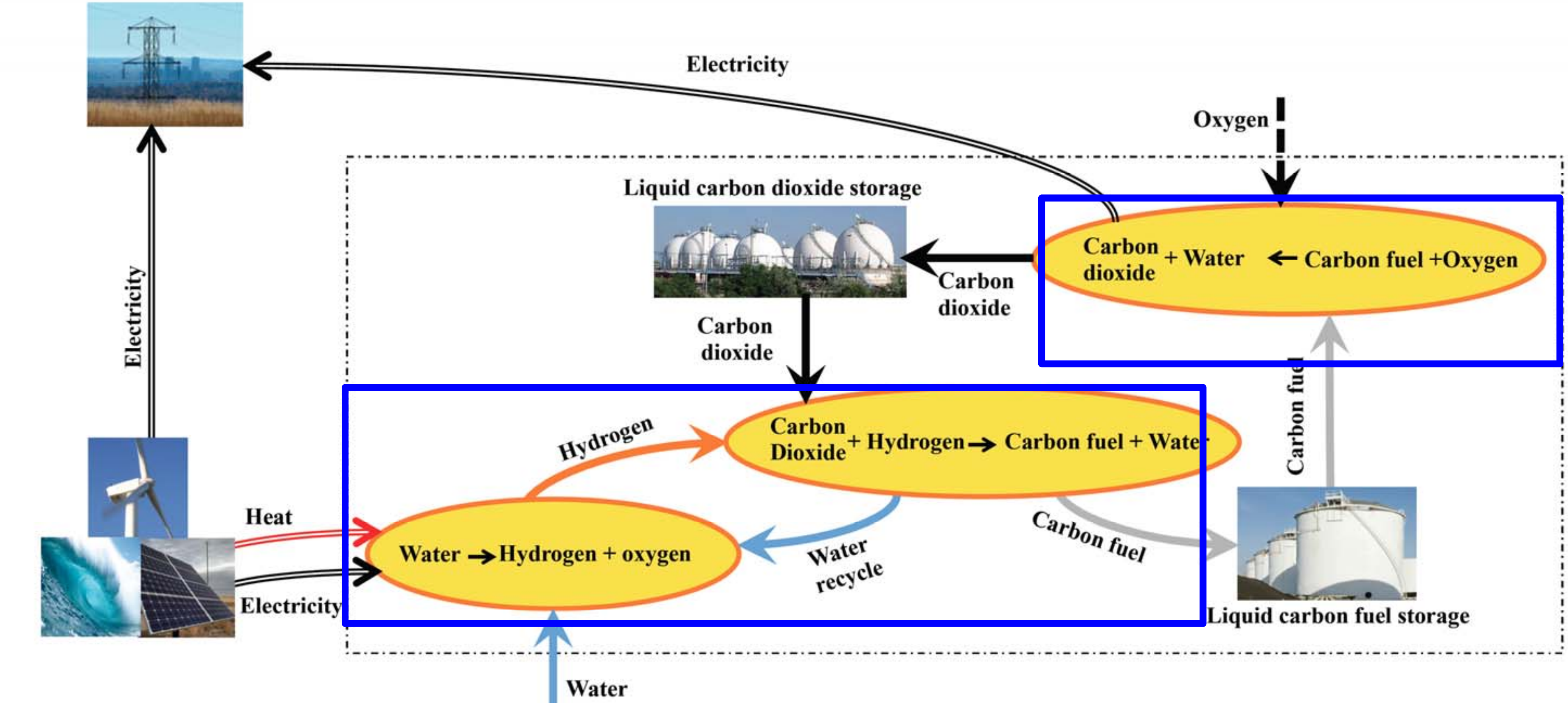
Hydrocarbons for Energy Storage
$CO_2+H_2 \rightarrow HC+H_2O$



- **Store as liquid to minimize volumes**
- **Avoid handling large volume of pressurized gas**

Reference: EPRI report on Storage Technologies, 2010
Hydro= pumped hydroelectric power, CAES= compressed air energy storage

Closed Carbon Energy Storage Cycle
Liquid CO_2 ←→ Liquid HC



Very little external carbon required as make up!

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Is there a Preferred HC for Energy Storage?

Consider the HC synthesis via

$CO_2 + H_2 \rightarrow HC + H_2O$

Metrics for HC Synthesis
$CO_2 + H_2 \rightarrow HC + H_2O$

- Exergy stored per mole carbon (kJ/mol C)
- Fraction of H_2 exergy recovered in the fuel (%)
- Exergy density as a liquid (GJ/m^3)

Metric #1: Exergy Stored per mole Carbon

Fuel	Exergy per carbon (kJ/mol C)
Methane	806
Ethane	723
Propane	692
Iso-octane	652
Cetane	640
Methanol	693
Ethanol	654
Dimethyl Ether (DME)	684

Metric #1: Exergy Stored per mole Carbon

Fuel	Exergy per carbon (kJ/mol C)
Methane	806
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Dimethyl Ether (DME)	684

- Methane stores the highest energy per carbon atom → least carbon supply

Metric #2: Fraction of H_2 Exergy Stored

Fuel	Fraction of H_2 exergy in fuel (%)
Methane	85.8
Ethane	88.0
Propane	88.4
Iso-octane	88.9
Cetane	89.0
Methanol	98.3
Ethanol	92.8
Dimethyl Ether (DME)	97.1

Metric #2: Fraction of H_2 Exergy Stored

Fuel	Fraction of H_2 exergy in fuel (%)
Methane	85.8
Ethane	88.0
Propane	88.4
Iso-octane	88.9
Cetane	89.0
Methanol	**98.3**
Ethanol	92.8
Dimethyl Ether (DME)	**97.1**

- **Methanol and DME top candidate for H_2 efficiency**

Metric #3: Exergy Density as Liquid

Fuel	Exergy density as liquid (GJ/m^3)
Methane	21.1
Ethane	25.2
Propane	25.9
Iso-octane	27.4
Cetane	25.5
Methanol	12.9
Ethanol	18.6
Dimethyl Ether (DME)	20.2

Metric #3: Exergy Density as Liquid

Fuel	Exergy density as liquid (GJ/m^3)
Methane	21.1
Ethane	25.2
Propane	25.9
Iso-octane	**27.4**
Cetane	25.5
Methanol	12.9
Ethanol	18.6
Dimethyl Ether (DME)	20.2

- **Octane has the highest density**

No single fuel favored in all three metrics..

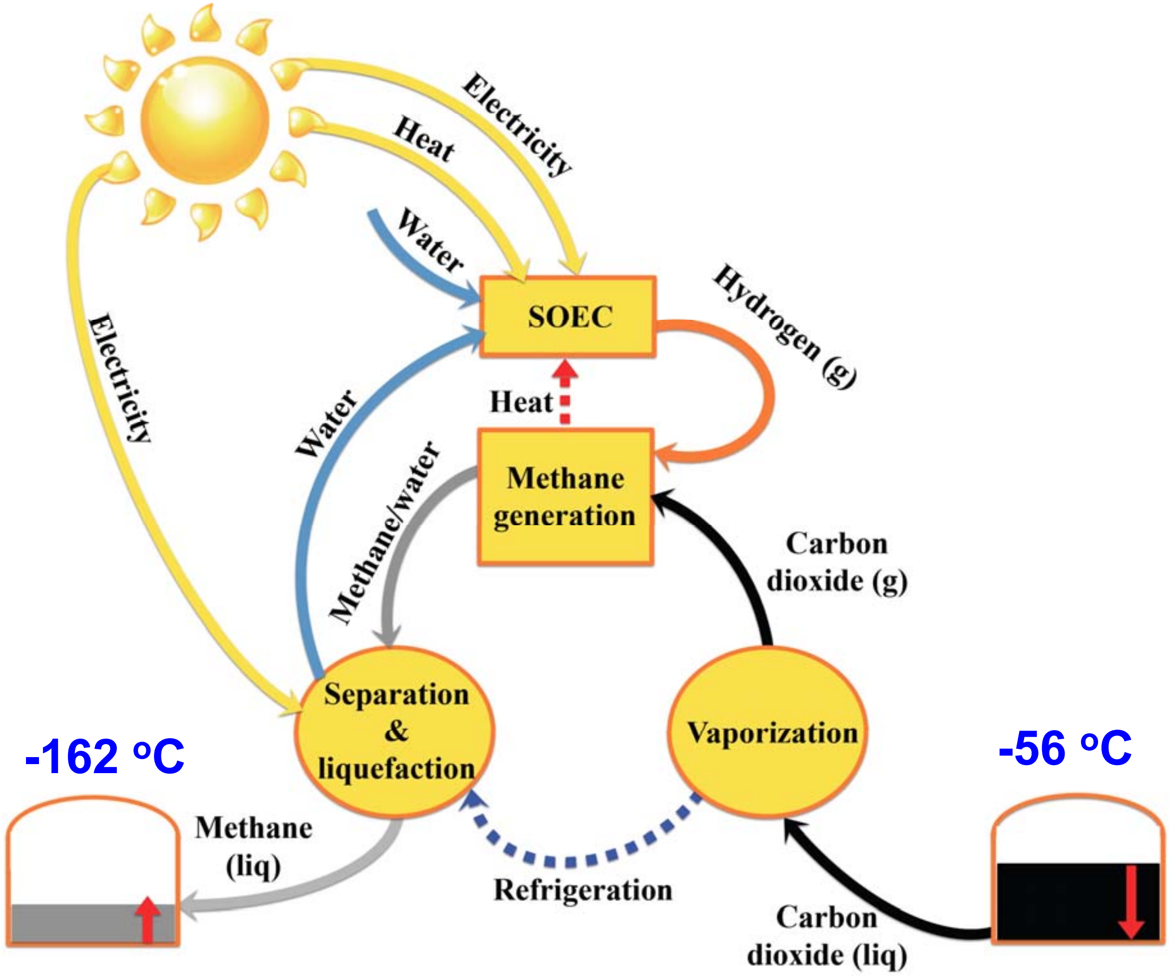
Trade-off between metrics needs to be optimized for different end uses

Among HC molecules..
… Consider the Use of Methane

Fuel	Exergy per carbon (kJ/mol C)
Methane	**806**
Ethane	723
Propane	692
Iso-octane	652
Cetane	640
Methanol	693
Ethanol	654
Dimethyl Ether (DME)	684

- **CH_4 → highest energy content per carbon**
- **Liquefaction energy penalty (-162 °C)**

Methane-cycle (Storage mode)

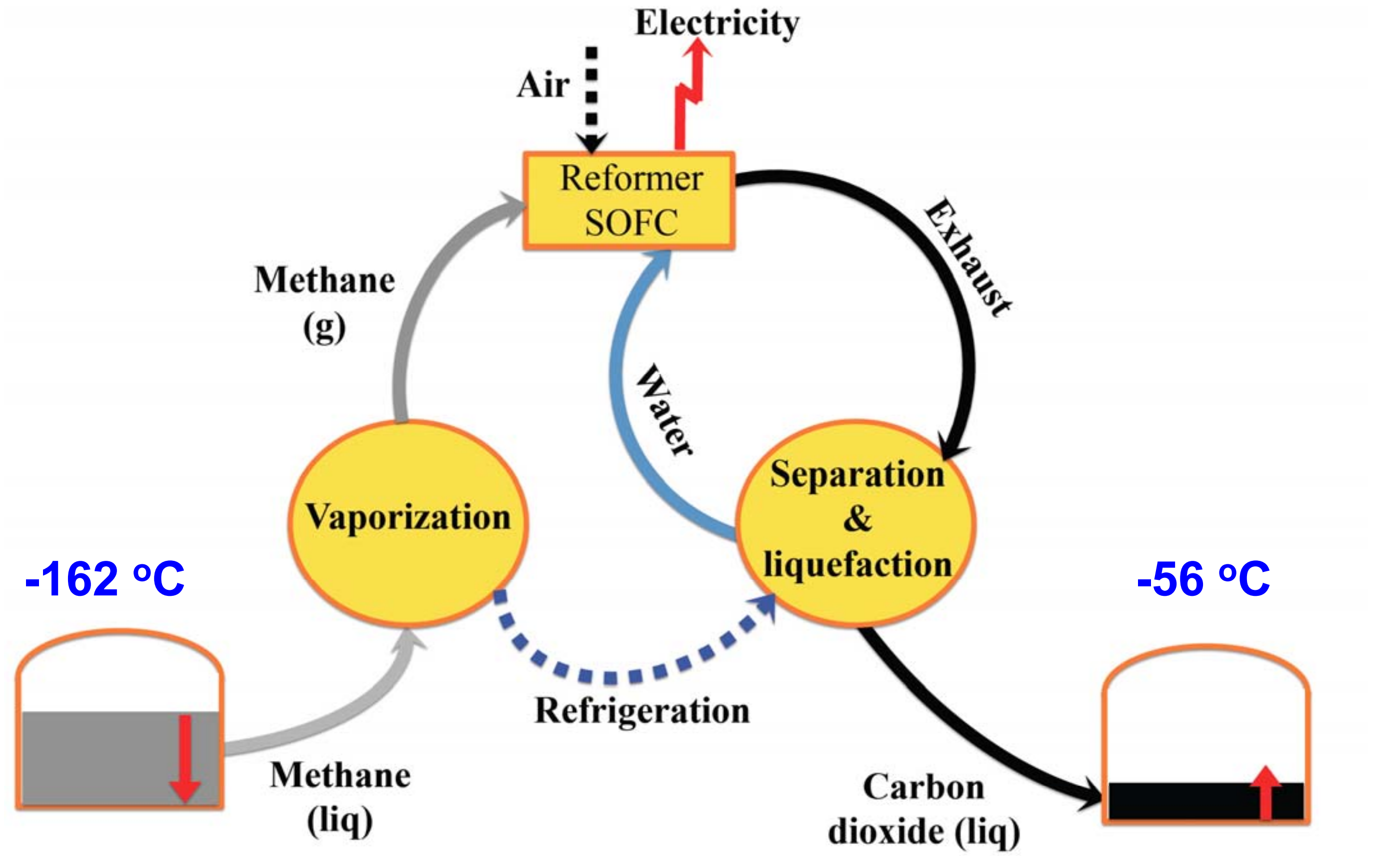


Minimize solar energy penalty of CH_4 liquefaction

SOEC=Solid Oxide Electrolysis

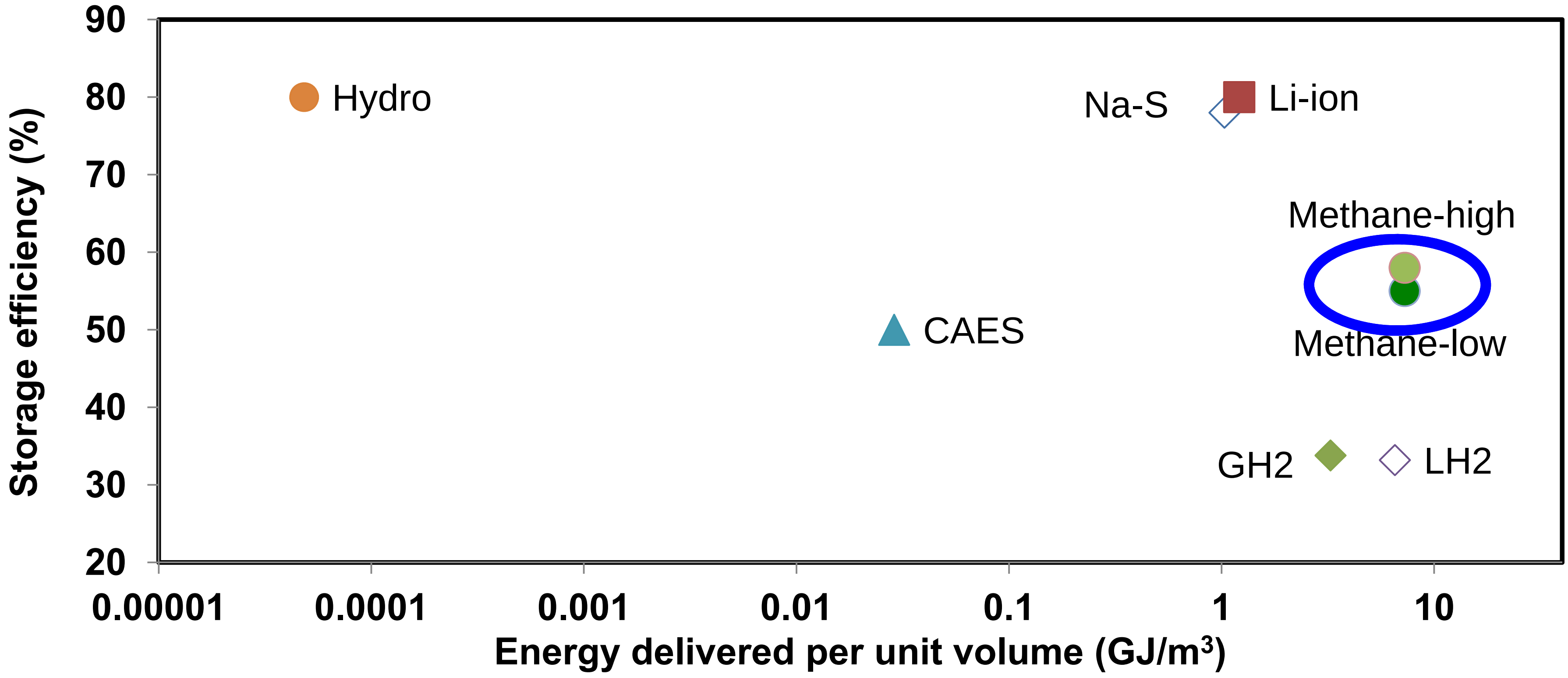
Methane-cycle (Delivery mode)

- **Solid Oxide Fuel Cell for H_2**



No power consumed for CO_2 capture and liquefaction!

Methane Storage Simulation Results



- **Efficiency:** **Methane superior to H_2**
- **Volume: Methane superior to other options**

Simulations carried out using Aspen Plus

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Similar efficiencies possible with Methanol (52-54%)

Improve Efficiency of Energy Use

Improve Efficiency of Energy Use

An Example: Multicomponent nonazeotropic distillation

Why is Separations Research Important?

- **40-70% of operating and capital cost of a typical chemical plant is due to separations**
- **90-95% of all separations in chemical and petrochemical plants are by distillation**
- **40,000 distillation columns in operation in US, and consume equivalent of ~ 1.2 million bbl of oil per day**
- **US refineries consume ~ 0.4 million bbl of oil per day for crude oil distillation alone**

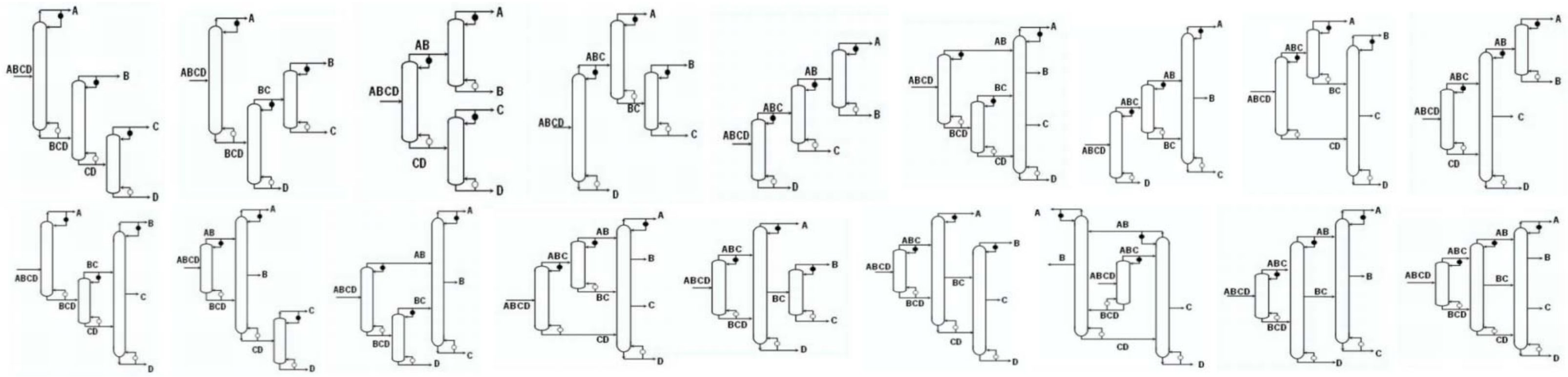
⬇

- **A saving of 20-50% in distillation energy could save 85-220 million bbl of oil equivalent per year (~ 8.5-22 billion dollars/year @ $100/bbl).**
- **These energy savings are comparable to the discovery of a new giant oil field (100 million bbl) every year!**

For a given application, our aim is to develop a method that allows a systematic search and identification of a separation system that is cost effective and energy efficient

Developed a Method to Generate Search Space of Basic Configurations

A Four Component Example



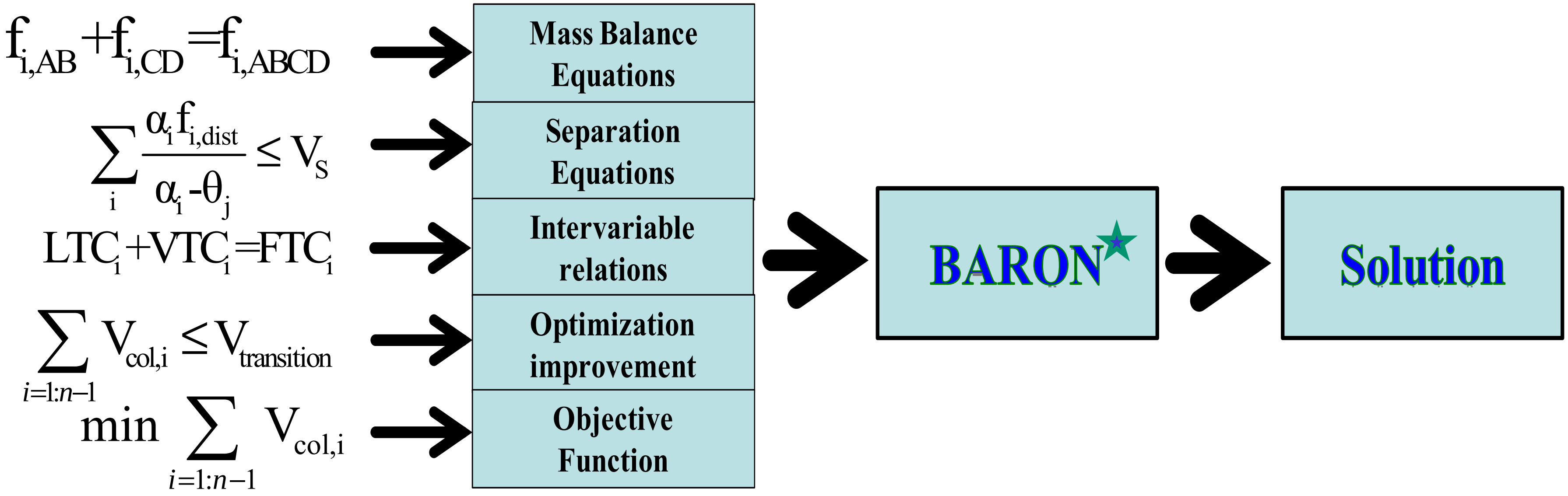
But, the number of configurations increase rapidly with number of components

Number of components in feed	Regular-column configurations	
	Without Thermal Coupling	With Thermal Coupling
4	18	134
5	203	5,925
6	4,373	502,539
7	185,421	85,030,771
8	15,767,207	29,006,926,681

…. and we still have to identify the best one !

Shah VH, Agrawal R.. AIChE Journal. 56, 1759 (2010)

NLP Formulation to Ranklist the Entire Search Space



$$f_{i,AB}+f_{i,CD}=f_{i,ABCD}$$

Mass Balance Equations

$$\sum_i \frac{\alpha_i f_{i,dist}}{\alpha_i-\theta_j} \le V_S$$

Separation Equations

$$LTC_i+VTC_i=FTC_i$$

Intervariable relations

$$\sum_{i=1:n-1} V_{col,i} \le V_{transition}$$

Optimization improvement

$$\min \sum_{i=1:n-1} V_{col,i}$$

Objective Function

BARON*

Solution

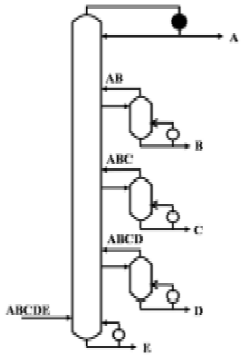
- **Succeeded in enumerating the useful distillation configurations for a given separation and rank them according to required vapor duty**
- **Solved the problem of developing a quick and reliable screening tool for multicomponent distillation**
- **Successfully applied our tool to proprietary separations at a major chemical company and identified several attractive configurations**

Nallasivam U, Shah VH, Shenvi AA, Tawarmalani M, Agrawal R. AIChE Journal. 59, 971 (2013)

***Branch-And-Reduce Optimization Navigator**

An Example

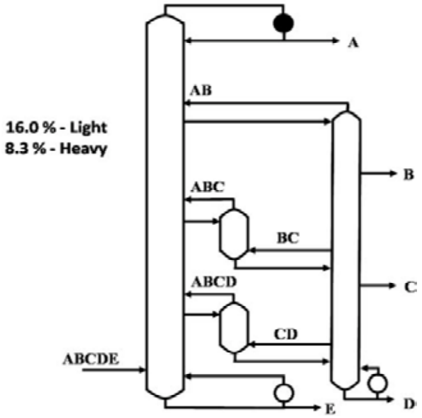
Petroleum crude distillation

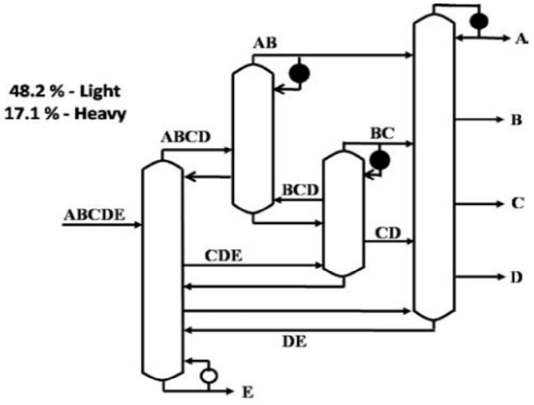


Current Configuration

- Petroleum crude distillation consumes huge amount of energy!
- Different refineries process different crudes, yet they have generally used the same configuration for 75+ years
- Identified hundreds of configurations which are potentially 15-50% more energy efficient than the above configuration

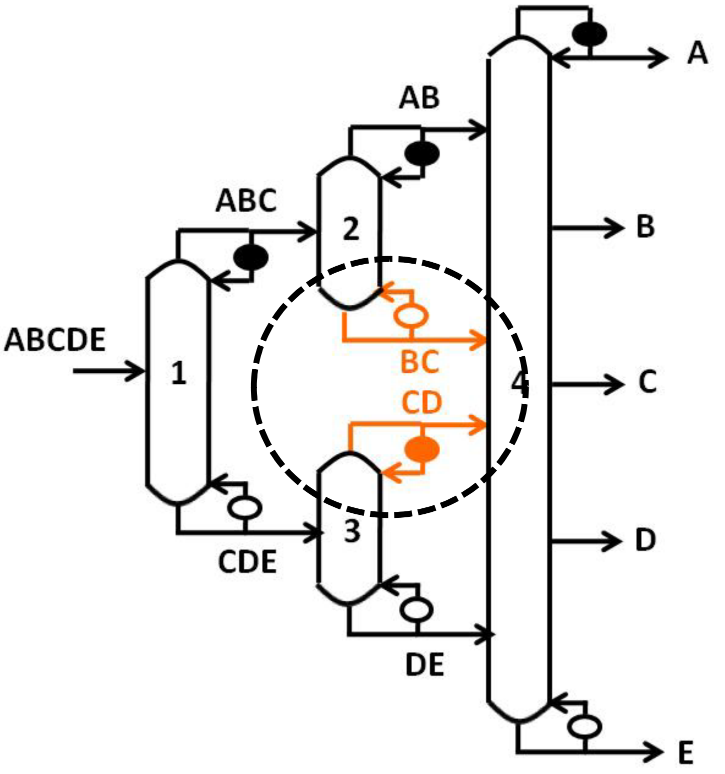
Example Energy Efficient Configurations



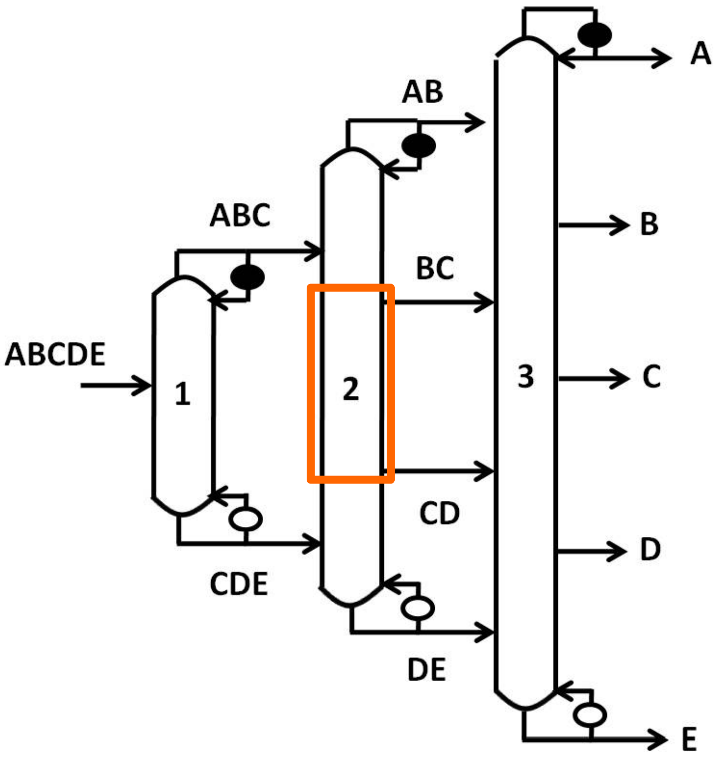


Shah VH, Agrawal R.. AIChE Journal. 56, 1759 (2010)

Identified Novel Heat and Mass Integrated Configurations



Regular-Column Configuration



Heat and Mass Integrated Configuration

Shenvi AA, Shah VH, Agrawal R. AIChE Journal. 59, 272 (2013)

Multicomponent Distillation Research is Still Vibrant and Fun!

Also Relevant to the Solar Economy

In Summary…

- **Solar economy requires energy and carbon efficient solutions**

- **Fuels and Chemicals**
    - SA biomass analogous to primary energy/carbon source
    - Preserve carbon - augmented biomass conversion
    - Simultaneous heat, mass and power process integration
- **Solar Hydrogen production**
    - STH_2 efficiency of 35-50% using membrane reactors
    - Superior to known electrolytic and single bandgap methods
- **Closed carbon cycles for grid-level energy storage**
    - Storage efficiency of 55-58% and much reduced volume
- **Use efficiency improvement in traditional areas will still be needed.** Example: Multicomponent Distillation
- **Energy modeling is multidimensional**

Acknowledgments

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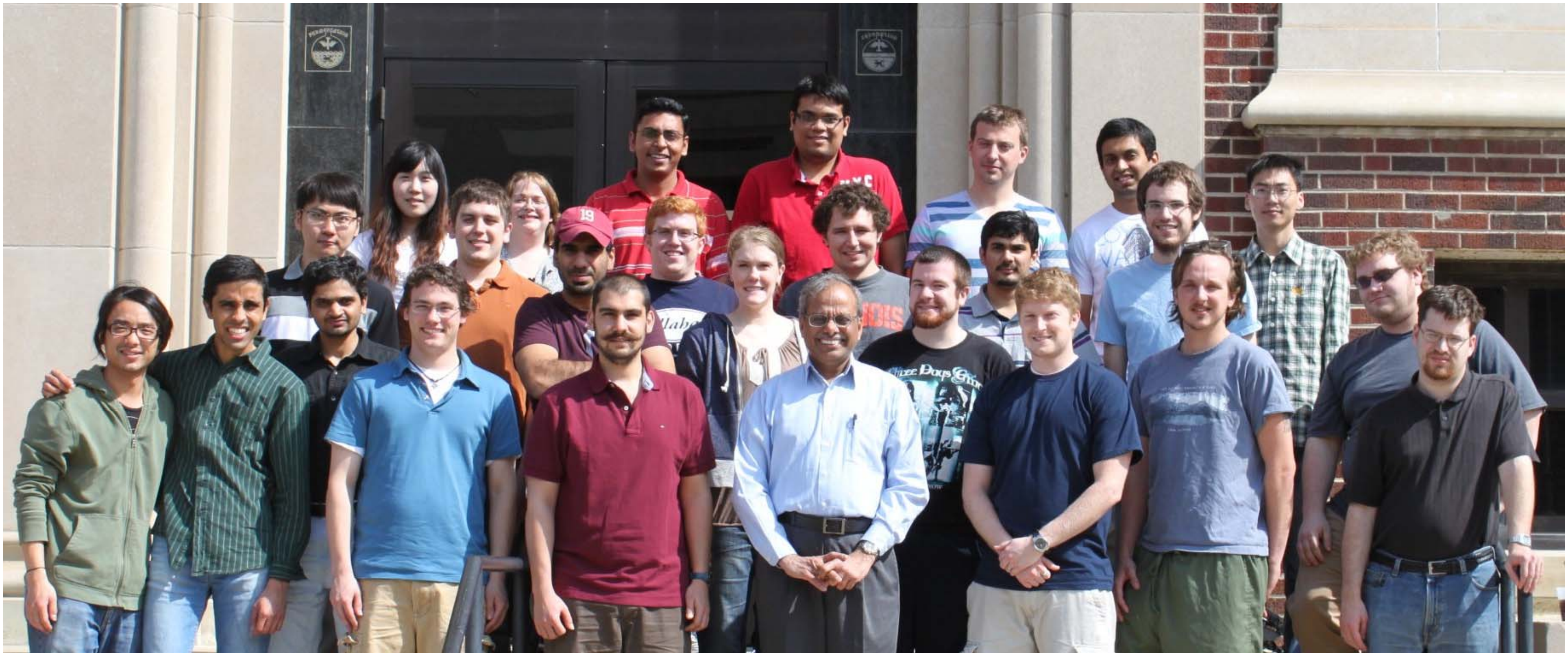
The Research Team



“A Great time to be a Chemical Engineer”

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....Thank you